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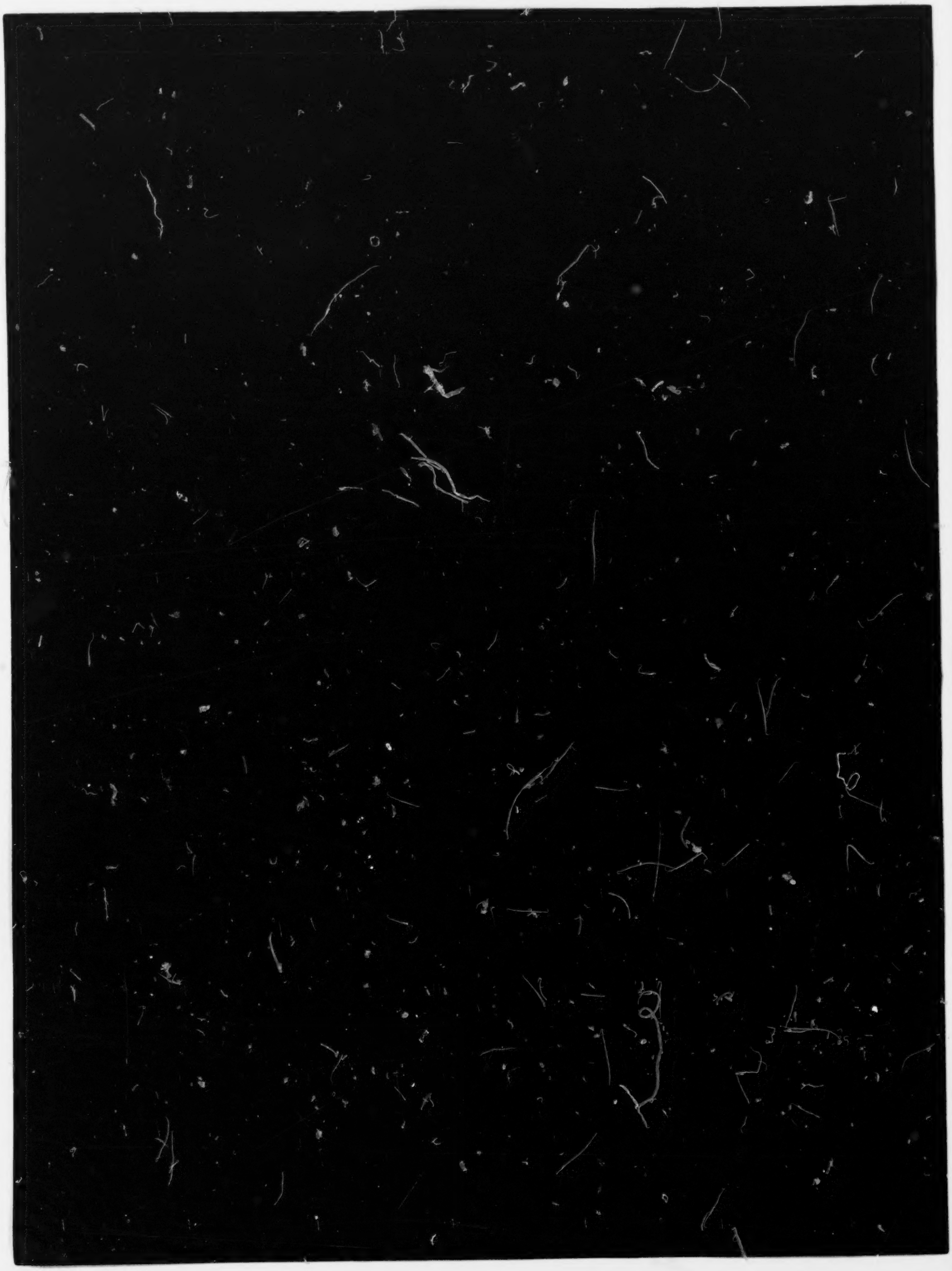

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27 Abstract

A laboratory study of the variables which affect the properties of the carbonate bonded coal refuse has been made. The carbonate bonding process utilizing coal refuse as a fill material consists of mixing coal refuse with water and lime hydrate, compacting the mixture, and reacting it with a carbon-dioxide-rich gas to form a coherent structure bonded by a matrix of calcite crystals. The resulting carbonate bonded coal refuse can be used in road building or as a coal refuse pile sealant to minimize acid mine water pollution.

Four types of coal refuse were investigated--a relatively unoxidized and highly oxidized bituminous coal refuse and a relatively unoxidized and highly oxidized anthracite coal refuse. It was found that compressive strengths of 2200 to 4400 psi were obtained for the four types of coal refuse investigated using up to 12 percent lime hydrate and 9 to 15 percent water. In general, the compressive streng of the carbonate bonded coal refuse increases with increasing lime hydrate content, reaction time and carbon dioxide concentration in the carbonate bonding reaction g

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Carbonate Bonding of Coal Refuse

by

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for the

ENVIRONMENTAL PROTECTION AGENCY
WATER QUALITY OFFICE

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ABSTRACT

A laboratory study of the operating variables which affect the properties of carbonate bonded coal refuse has been made. The carbonate bonding process utilizing coal refuse as a fill material consists of mixing coal refuse with water and lime hydrate, compacting the mixture, and reacting it with a carbon-dioxide-rich gas to form a coherent structure bonded by a matrix of calcite crystals. The resulting carbonate bonded coal refuse can be used in road building or as a coal refuse pile sealant to minimize acid mine water pollution.

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The air and water permeability of carbonate bonded coal refuse was found to be comparable to concrete. An approximate cost comparison between carbonate bonded coal refuse and other construction materials and techniques indicated that the carbonate bonding process utilizing coal refuse is the most economical means available for coal refuse pile sealing and road building.

This report was submitted in fulfillment of Research Grant No. 14010FOA between the Environmental Protection Agency and the Applied Technology Division of Black, Sivalls & Bryson, Inc.

Key Words: Carbonate bonding, coal refuse, coal refuse binder, refuse pile sealant, pollution abatement, road building

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CONCLUSIONS

In general, the excellent properties of carbonate bonded coal refuse obtained in this study indicate great potential for carbonate bonding as a means of eliminating acid mine drainage by coal refuse pile sealing and utilization of coal refuse in road building. In particular, the following conclusions may be drawn from the results of this study:

1. Compressive strengths of 2200 to 4400 psi were obtained for the coal refuse types under investigation using up to 12 percent lime hydrate content and water contents in the range of 9 to 15 percent. The compressive strength of the carbonate bonded coal refuse increases with increasing lime content, carbonate bonding reaction time and carbon dioxide concentration in the carbonate bonding reaction gas. The compressive strength also increases with decreasing coal refuse particle size due to a wider particle size distribution.

2. Air and water permeability of carbonate bonded coal refuse was found to be comparable to concrete.

3. An approximate cost comparison indicated that carbonate bonded coal refuse is significantly less expensive than other construction materials for sealing coal refuse piles or for load bearing applications. The cost of carbonate bonding 2-inch to 15-inch thick layers of coal refuse was estimated to range from $0.83 to $2.48 per square yard. For sealing coal refuse piles, a 6-inch carbonate bonded layer will be comparable to a four foot layer of dirt. Sealing with a four foot layer of dirt is estimated to cost $1.33 whereas a 6-inch thick carbonate bonded seal was conservatively estimated at $1.28 per square yard. For secondary road construction, a 6-inch layer of carbonate bonded coal refuse would cost approximately $1.28 as compared to $4.68 per square yard for a 2-inch asphalt, 4-inch subbase road. Carbonate bonded coal refuse used as a subbase in road construction is significantly less expensive than conventional materials. A 4-inch subbase of carbonate bonded coal refuse would cost $1.05 as compared to $1.56 per square yard for conventional materials. If a 12-inch thick layer of carbonate bonded coal refuse is covered with a 2-inch layer of asphalt to produce a first class road, the cost would be $5.17 as compared to $7.62 per square yard for a first class asphalt road.

4. Laboratory results indicate that commercial application of the carbonate bonding process should present no unusual problems. Although the particle size of the coal refuse to be carbonate bonded affects the resulting compressive strength, there will be little or no preparation required for the coal refuse prior to carbonate bonding. Compressive strength did not exhibit severe changes with water content in the 9 to 15 percent range. Consequently, there will be no need for critical control of the water content in the commercial application of this process. In addition, it was found that compressive strength was not substantially increased by utilizing pure carbon dioxide; therefore, an inexpensive burner will suffice as a source of carbon dioxide in the application of the process.

RECOMMENDATIONS

The proposed applications for carbonate bonded coal refuse and the suggested commercial process techniques are postulated on the encouraging but limited results of this study. Additional work will be required to demonstrate the carbonate bonding process on a large scale. Depending on the availability of funds, it is recommended that at least one of the following three process demonstration studies be conducted.

1. It is recommended that a small coal refuse plot be paved to demonstrate the commercial utility of the process as a coal refuse pile sealant and road building material. For demonstration purposes, the test plot should be a minimum of 20 feet by 20 feet. Based on the results from the demonstration plot, an engineering evaluation of the process will be made with pertinent recommendations as to further application.

2. It is recommended that the process be demonstrated on a full-size actual coal refuse pile. By sealing the pile, not only will acid water formation be prevented but the necessary techniques for large scale construction could be developed. Based on results of this demonstration, an engineering evaluation of the process will be made, construction standards and procedures will be developed and process costs established, for future application of the process.

3. It is recommended that the process be demonstrated by construction of a secondary road in the vicinity of a coal refuse pile. This demonstration will reduce the size of the selected coal refuse pile, provide additional roads for the community, establish road building costs, and develop road building techniques for application of the carbonate bonding process.

4. As a part of any of the above projects, a study should be undertaken to determine feasibility of producing lime hydrate suitable for carbonate bonding from limestone available near coal refuse sources. The purpose of this work will be to minimize cost of transporting lime hydrate to point of use.

5. An additional part of any of the above programs should include a study of material stability in an actual acid mine drainage environment.

Once the above demonstration studies are completed, carbonate bonding costs will have been established

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INTRODUCTION

The project involves the investigation of a process that has several applications in combating water pollution and other problems created by coal refuse piles. The need for such a process arises from the fact that as rain water percolates down through the spoil bank, the reaction between pyrites, air, and water generates acid-forming constituents which are carried in the water table or streams surrounding the locale. Thus, to minimize this serious pollution problem, an effective process for sealing off spoil banks or utilizing coal refuse is required.

One application of the process is the sealing of coal refuse piles with a layer of carbonate-bonded refuse to exclude air and moisture from the pile, and thus eliminate the formation of acid drainage. A second application of this process is the elimination of refuse piles by utilizing the refuse material as filler in the construction of carbonate bonded road pavement and in the manufacture of low-cost bricks and similar products.

In this process, lime hydrate is throughly blended with coal refuse (or spoil bank materials) and then treated with carbon dioxide to form strong calcium carbonate (calcite) crystals. The calcite crystals act as a cementing matrix that turn the coal refuse into a coherent and impervious structure. The carbonate bonding process relies on the simple reaction that occurs between carbon dioxide and lime hydrate. In the reaction:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

carbon dioxide reacts with lime hydrate to produce calcium carbonate (calcite) and water. The reaction is well known and occurs naturally upon the exposure of lime hydrate to the atmosphere. However, the rate of conversion of lime hydrate to calcium carbonate is relatively slow because of the small percentage of carbon dioxide contained in the air. It is of interest to note that although the reaction in air is slow, the reaction proceeds rapidly in concentrated carbon dioxide. Because of its high strength, the calcite crystal affords an opportunity for exploiting lime hydrate as a cementing material to bind coal refuse into a coherent structure.

Most of the experimentation prior to this work has been conducted with various types of soils and not with coal refuse materials. Therefore, this bench-scale experimental study was undertaken to determine the operating parameters for generating a strong carbonate bonded coal refuse and to determine the feasibility of the carbonate bonding process for the elimination of acid mine water formation from coal refuse piles. In particular, the effects of lime hydrate content, moisture content, partial pressure of carbon dioxide in carbonating gas, carbonation time, and the external surface area of coal refuse on the compressive strength

of the coal refuse were determined. In addition, the air and water permeability and the freeze-thaw resistance were determined for carbonate bonded coal refuse.

Before proceeding with a discussion of the experimental work, it would be well to discuss some of the theoretical aspects of the carbonate bonding reaction and the results from prior experimentation with other fill materials. The relationship between the compressive strength of carbonate bonded materials and process operating variables is as yet not fully understood. Prior experimentation on soils, clays, and sands indicatesthat compressive strength increases as:

(1) The particle size of the fill material and lime hydrate decreases

(2) An optimum water content is selected for each specific fill material

(3) The external surface area of the fill material increases

(4) The carbon dioxide partial pressure in the carbonating gas is balanced so that the rate of heat generation within the composite equals the rate of heat loss to the surrounding gas phase

(5) The time of carbonation increases, and

(6) The lime hydrate concentration increases

Decreasing the particle size (along with a wider particle size distribution) of the fill material decreases the porosity of the composite which is to be carbonate bonded. Decreasing the porosity yields a more dense composite and enhances the formation of a continuous calcite matrix. As the compressive strength of the composite is mainly a function of the continuity of the calcite crystal structure, a minimum porosity condition increases the strength of the carbonate bonded material.

As the surface area of the lime hydrate increases, its rate of solution in water is increased. This causes the carbon dioxide to react with a saturated lime hydrate solution and results in a rapid precipitation of a fine calcite crystal matrix. The rapid formation of a multitude of crystals enhances additional crystaline growth so that bridging and growth can occur between crystals with a resulting increase in strength.

In general, the greater the external specific surface area of the fill material, the greater will be the rugosity or roughness of the surface of the particles. This condition provides numerous bridging channels between particles for the growth of calcite crystals and increases the strength of the carbonate bonded material.

The effect of the partial pressure of carbon dioxide in the carbonating gas on the carbonation reaction is directly related to the gas phase mass transfer of carbon dioxide to the liquid film. Prior experimentation has

shown that the rate of the carbonate bonding reaction is directly proportional to the partial pressure of carbon dioxide. Since the carbonate bonding reaction is highly exothermic, the heat released during this reaction can be controlled by varying the partial pressure of carbon dioxide in the gas phase. Depending upon the water content, and the thermal characteristics and packing of the fill material, it is possible to crack the resulting carbonate bonded material by causing the reaction to occur too rapidly. Due to a high carbonation rate sufficient heat is generated to produce steam within the interior of the composite. If the packing is too dense, rapid steam evolution from the carbonate bonded material is inhibited and can result in sufficient internal pressure to crack or rupture the composite. Consequently, the partial pressure of carbon dioxide must be optimized so that internal pressure cracks are not generated and the strength characteristics of the carbonate bonded material can be maintained.

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RAW MATERIALS USED

Four types of coal refuse were investigated, a relatively fresh (unburnt) bituminous, a highly oxidized (burnt) bituminous, a relatively fresh unoxidized (unburnt) anthracite, and a highly oxidized (burnt) anthracite. The bituminous samples were obtained from the Kittaning coal seam of the Roaring Creek Coal Company* in Norton, West Virginia. The anthracite samples were obtained from the Reading Coal Company* located in Pottsville, Penna. Each of the samples was initially screened to remove lumps and yield a -10 mesh sample. A portion of the -10 mesh sample was subjected to grinding to obtain a -20 mesh and -60 mesh size fraction for use in subsequent experimentation. The screen analysis for the -10, -20, and -60 mesh samples for each type of coal refuses is presented in Table I.

TABLE I

Screen Analysis of Coal Refuse

UNBURNT BITUMINOUS

Screen	-10 Mesh Sample	-20 Mesh Sample	-60 Mesh Sample
20	69.7%		
40	15.6%	48.9%	
60	4.7%	18.6%	
100	3.4%	11.3%	27.8%
200	3.5%	8.4%	56.6%
325		4.5%	6.3%
PAN	3.1%	8.3%	9.3%

BURNT BITUMINOUS

Screen	-10 Mesh Sample	-20 Mesh Sample	-60 Mesh Sample
20	38.1%		
40	23.4%	30.9%	
60	8.3%	16.7%	
100	8.3%	12.4%	52.8%
200	9.2%	12.0%	39.7%
325		8.5%	4.2%
PAN	12.7%	19.5%	3.3%

UNBURNT ANTHRACITE

Screen	-10 Mesh Sample	-20 Mesh Sample	-60 Mesh Sample
20	57.8%		
40	20.8%	43.1%	
60	6.6%	19.6%	
100	5.0%	10.7%	45.7%
200	4.4%	10.0%	50.6%
325		6.5%	3.5%
PAN	5.4%	10.1%	.2%

BURNT ANTHRACITE

Screen	-10 Mesh Sample	-20 Mesh Sample	-60 Mesh Sample
20	43.9%		
40	22.9%	33.5%	
60	9.6%	19.4%	
100	8.5%	13.8%	34.4%
200	8.2%	13.0%	61.3%
325		7.2%	2.3%
PAN	6.9%	13.1%	2.0%

In Table II is shown the external surface area (cm^2/gram) for each size fraction and type of coal refuse.

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* Mention of commercial products or organizations does not imply endorsement by EPA

TABLE II

Specific Surface Area of Coal Refuse

Sample	Surface Area, cm^2/gram -10 Mesh	-20 Mesh	-60 Mesh
Unburnt Bituminous	163	763	2249
Burnt Bituminous	998	1231	1959
Unburnt Anthracite	186	705	1775
Burnt Anthracite	294	535	1533

The external surface area was determined using an air permeability technique in which the Carman-Kozeny equation was used to relate the external surface area to the pressure drop of air passing through a packed bed of coal refuse.

The lime hydrate used in these experiments is a dolomitic hydrate and was obtained from the Ohio Lime Company,* Woodville, Ohio. A typical analysis for this superfine lime hydrate is presented in Table III.

TABLE III

Chemical and Screen Analysis of Dolomitic Lime Hydrates

TYPICAL CHEMICAL ANALYSIS

	Guaranteed Minimum	Average
Calcium Oxide	46.87%	49.20%
Magnesium Oxide	33.98%	34.00%
Calcium Hydroxide	62.04%	65.00%
Silicon Dioxide	.23%	.20%
Iron Oxide	.07%	.10% max.
Aluminum Oxide	.16%	.40% max.

TYPICAL SCREEN ANALYSIS

Fineness			
Passing	100	U.S. Mesh	100.00%
Passing	200	U.S. Mesh	99.78%
Passing	300	U.S. Mesh	99.64%
Passing	325	U.S. Mesh	99.50%

60% finer than 20 microns
20% finer than 14 microns
8% finer than 10 microns

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This type of lime hydrate was selected because prior experimentation has shown it to be suitable for carbonate bonding. Other types of limestones might have been used with more or less success; however, an investigation of the effect of lime hydrate type on the quality of carbonate bonded coal refuse was beyond the scope of this study.

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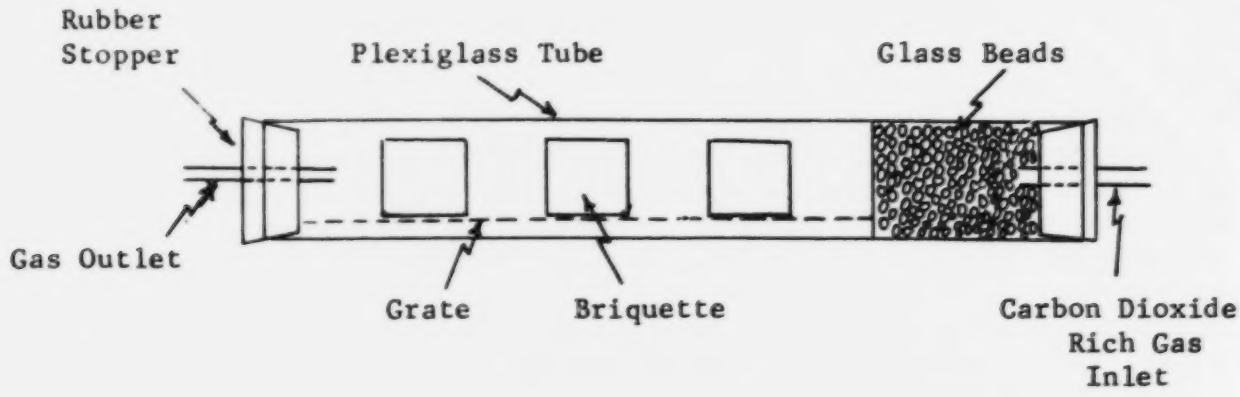
CARBONATE BONDING TECHNIQUE AND APPARATUS

The preparation of coal refuse for carbonate bonding consisted of mixing in sufficient water to bring the water content to a specified value. This mixture was allowed to stand at least 24 hours to permit an equilibrium of the water throughout the mixture. Lime hydrate was then thoroughly blended into the coal refuse. To permit a rapid scanning of parameters and to minimize the quantities of materials and size of the carbonate bonding apparatus, the lime hydrate coal refuse mixture was placed in a small die and compacted to yield a 1 1/8 inch diameter by 1 inch high briquette. A compaction load of 6000 psi was used to form the briquettes of these experiments. In the commercial application of the carbonate bonding process lower compaction loads would be used in the order of 1000 psi. It was decided to use higher compaction load for experimental purposes so that the briquettes would not have loose edges and would be of exact dimensions. The briquetting pressure was then removed and the soft, easily crushed briquette was placed in a reactor and contacted with a carbon dioxide rich gas for a specified time. The briquette was removed and the compressive strength determined. In this manner, the compressive strength of a carbonate bonded coal refuse was determined for a particular coal refuse and particle size, lime hydrate and water content, carbon dioxide concentration and carbonate bonding time.

The carbonate bonding reactor is shown schematically in Figure 1. Tanks of carbon dioxide and nitrogen were used as the source of these gas constituents. Experiments were run with carbonate bonding gas containing 20, 60, and 100 percent carbon dioxide concentrations. The carbon dioxide and nitrogen were individually metered, combined in a mixing chamber, and admitted to the carbonate bonding reactor. The reactor consisted of a plexi-glass tube, 2 inches I.D. by 24 inches long. The formed briquettes were arranged on a metal grate which slid into the reactor tube. Six reactor tubes were used to permit segregation of the various coal refuse briquettes. For all experimentation, a gas flow of 0.55 standard cubic feet per minute was used which resulted in a superficial gas velocity of 0.43 feet per second in each individual reactor tube.

The procedure used to carbonate bond the coal refuse briquettes consisted of placing the briquettes in the reactor tubes. The flow rates of nitrogen and carbon dioxide were then adjusted to the desired flows. During this initial adjustment the flow of the resulting gas mixture was made to bypass the reactor tubes. Once the desired gas mixture was obtained, a stop watch was started and the bypass closed causing the gas mixture to enter the reactor tubes. When the specified carbonate bonding reaction time was reached the carbon dioxide was cut off and the nitrogen allowed to flow through the reactor tubes for several additional minutes to flush out all remaining reaction gas. The carbonate bonded coal refuse briquettes thus formed were removed and either tested for their compressive strength or subjected to other tests.



Reactor System

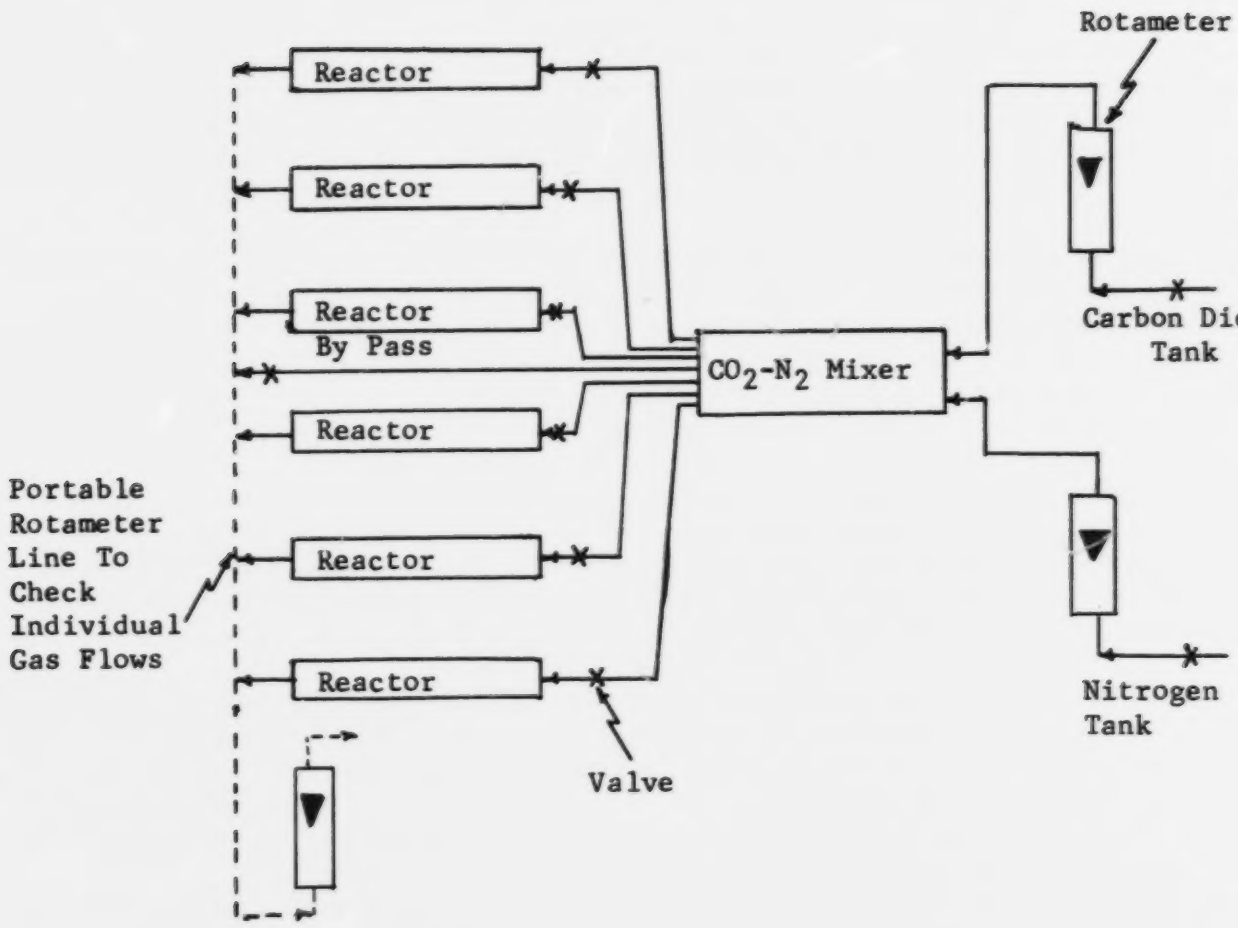


FIGURE 1-CARBONATE BONDING REACTOR SYSTEM

EXPERIMENTAL LABORATORY STUDY

For convenience in presentation, the experimental laboratory study was divided into two categories--those experiments which pertain to the effect of various carbonate bonding parameters on the compressive strength of carbonated coal refuse and those experiments which were used to determine the physico-chemical properties of the resulting carbonate bonded coal refuse. In the first category, the effect of coal refuse type and particle size, lime hydrate and water content, carbonate bonding reaction time, and carbon dioxide concentration, on the compressive strength of the carbonate bonded coal refuse were ascertained. In addition, the effect of curing time on compressive strength will be discussed. The curing time is defined as the total time elapsed after carbonate bonding is officially completed (removal from reactor). During this study it was observed that the compressive strength increased significantly for some time after carbonation. Included in the second category of experiments were air and water permeability and freeze-thaw testing of carbonate bonded coal refuse.

Effect of Carbonate Bonding Parameters on Compressive Strength

The structural integrity of carbonate bonded coal refuse is a prime consideration of any of its possible applications. Since the process is being considered for the sealing of coal refuse piles, the sealing layer must have sufficient strength to withstand vehicular and pedestrian traffic. Consequently, in this short feasibility study it was expedient to select one strength property as representative of the structural integrity of the resulting carbonate bonding material. For this study compressive strength was selected because of its applicability toward the intended use of the carbonate bonding process and because of its ease of determination. The determination of the compressive strength of a solid material is normally accomplished under conditions in which the rate of application of load is precisely controlled. In view of the limited objectives of this study and the numerous uncontrollable parameters associated with carbonate bonding, this degree of precision was deemed unnecessary. Consequently, a simple technique was devised to determine compressive strength. The briquette was placed in a press and the press plates closed until a small load resulted on the briquette. The press operator then applied a slow but approximately reproducible rate of loading on the briquette until failure occurred. The load at failure was recorded and used to calculate the compressive strength of the briquette.

Effect of Lime Hydrate Content on Compressive Strength

To determine the effect of lime hydrate content on the compressive strength of the resulting carbonate bonded briquettes, a series of carbonate bonded coal refuse briquettes were prepared in which the lime hydrate content was varied between 3 and 12 percent by weight and the water content varied in the rangeof 3 to 12 percent by weight. From

prior experimentation with other fill materials (soils, ores etc.) it has been found that optimum carbonate bonding strength normally occurs in these ranges of lime hydrate and water. The percent of water was based on the original dry weight of the coal refuse (and thus corresponds to the moisture that will be measured in exposed refuse piles) whereas the percent of lime hydrate was based on the weight of wet coal refuse. The compressive strength as a function of the percent of lime hydrate at the optimum percent of water is shown in Figures 2 to 5 for each coal refuse (-10 mesh). For these experiments a 20 percent carbon dioxide gas mixture and a 4 hour carbonate bonding reaction time was used. Also, the compressive strength was determined immediately after carbonate bonding was completed (zero curing time). Figures 2 to 5 clearly indicate that the compressive strength increased as the percent of lime hydrate increased for each of the refuse materials studied.

Effect of Curing Time on Compressive Strength

In Figures 2 to 5 it is seen that the maximum compressive strength obtained for each coal refuse was about 1500 psi at 12 percent lime hydrate, and maximum strengths occurred at 12, 12, 9, and 12 percent water for unburnt and burnt bituminous and unburnt and burnt anthracite coal refuse respectively. The resulting compressive strengths were rather low judging from prior experimental results using other fill materials for carbonate bonding which yielded compressive strengths in excess of 2000 psi. Consequently, additional experiments were conducted to determine if there is a curing time effect on compressive strength.

To show the effect of curing time on compressive strength, carbonate bonded briquettes were prepared in the usual manner except that the compressive strength was determined as a function of the time elapsed after carbonate bonding was completed. This was done for each coal refuse at 12 percent lime hydrate and the optimum percent of water. For these experiments the -10 mesh particle size fraction, a 100 percent carbon dioxide gas mixture and a 4 hour carbonate bonding time were used. Compressive strengths were determined at various times after carbonate bonding was completed for a total time of 600 hours. In Figure 6 the compressive strength as a function of curing time for unburnt bituminous which is shown is typical for all the coal refuses studied. The compressive strength increases significantly during the first 150 hours of curing time and then levels off to a relatively constant value. Specifically, for the unburnt bituminous coal refuse, the compressive strength increased from about 1500 psi to 4400 psi after a curing time of approximately 150 hours. In order to make these findings applicable to a wide variety of coal refuses, Figure 7 was prepared and is a plot of the reduced compressive strength, defined by $(S_t - S_o)/(S_{oo} - S_o)$, as a function of the curing time in hours: where,

S_t = compressive strength at any time

S_o = compressive strength at time zero (immediately after carbonate bonding)

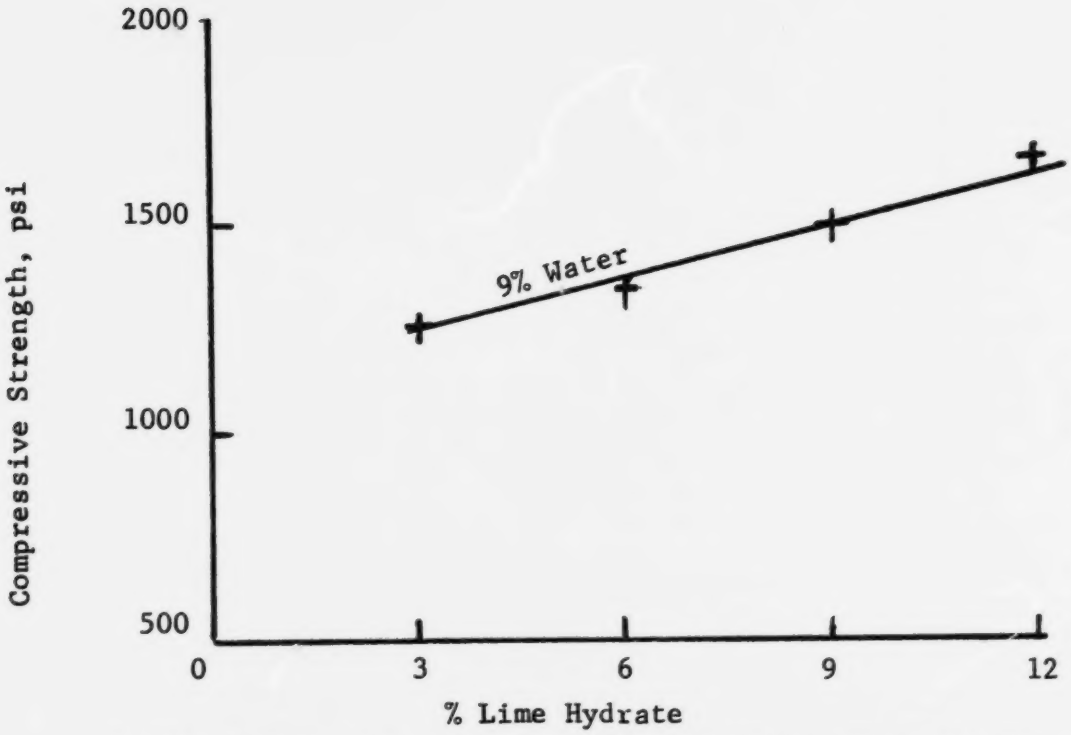


FIGURE 2-EFFECT OF LIME HYDRATE CONTENT ON COMPRESSIVE STRENGTH FOR UNBURNT BITUMINOUS COAL REFUSE

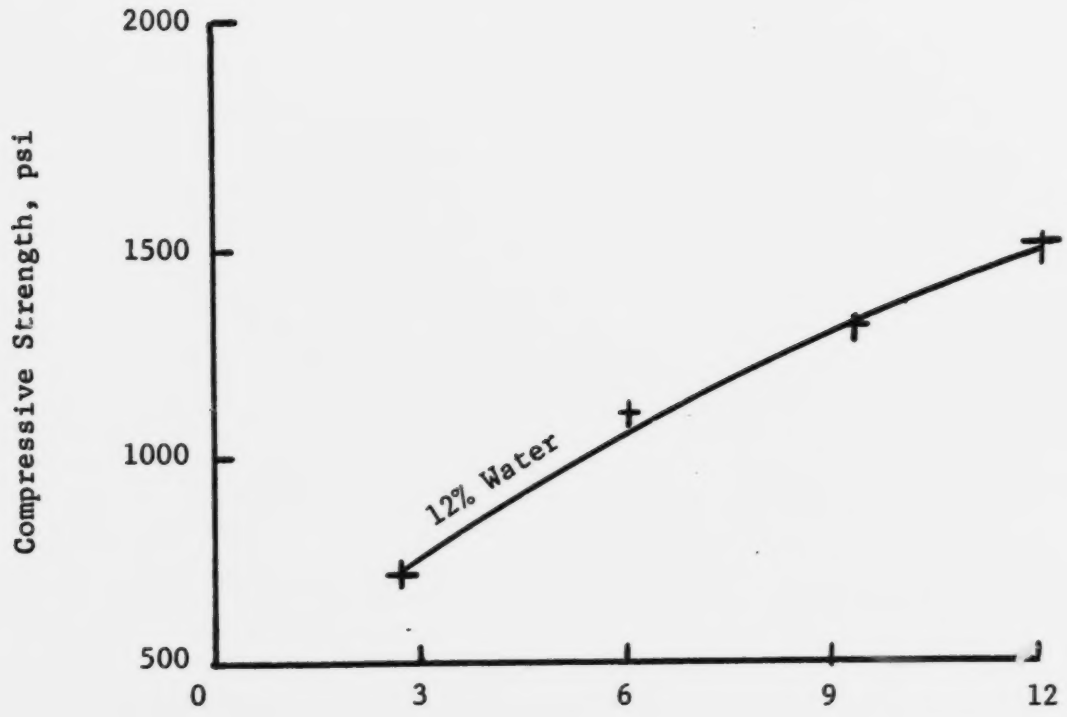


FIGURE 3-EFFECT OF LIME HYDRATE CONTENT ON COMPRESSIVE STRENGTH FOR BURNT BITUMINOUS COAL REFUSE

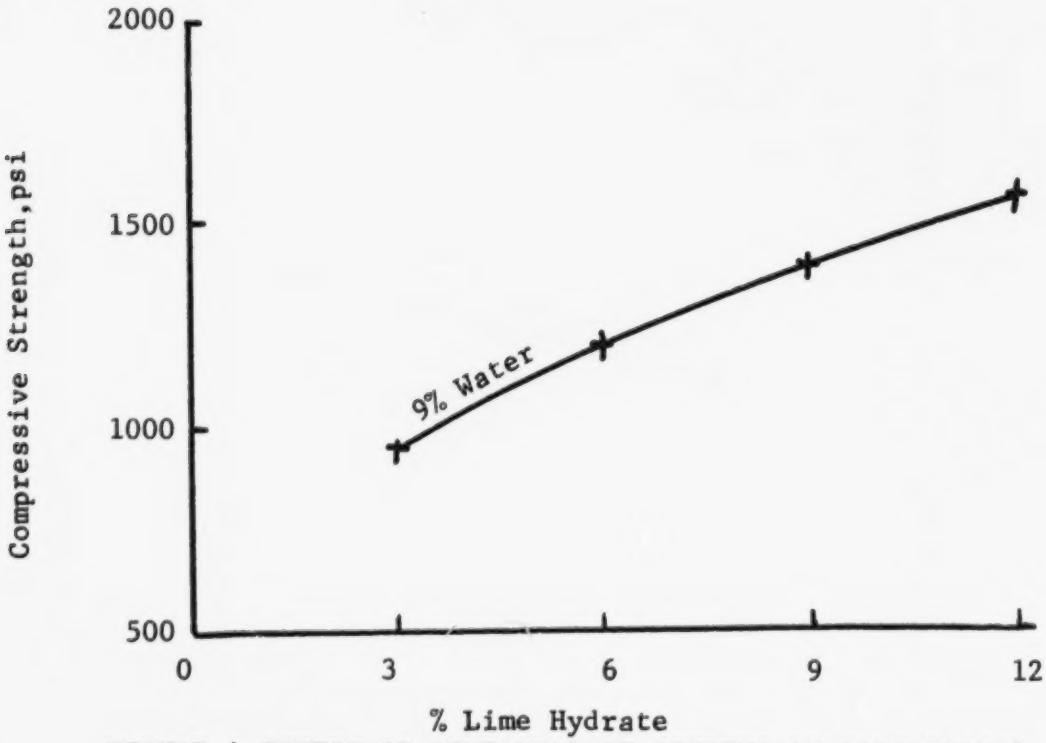


FIGURE 4-EFFECT OF LIME HYDRATE CONTENT ON COMPRESSIVE STRENGTH FOR UNBURNT ANTHRACITE COAL REFUSE

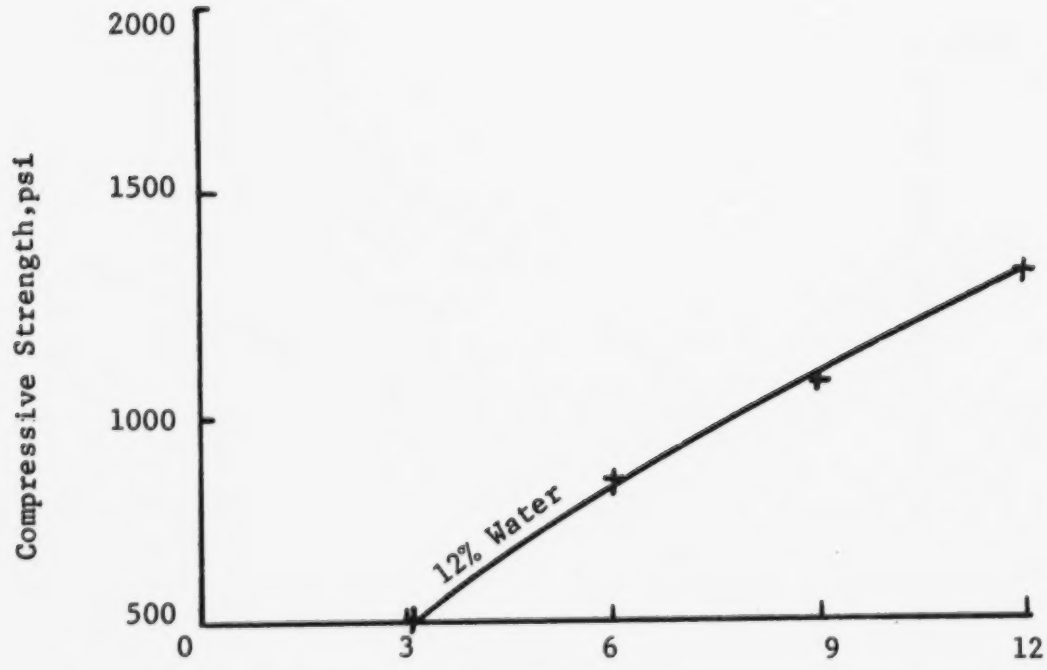


FIGURE 5-EFFECT OF LIME HYDRATE CONTENT ON COMPRESSIVE STRENGTH FOR BURNT ANTHRACITE COAL REFUSE

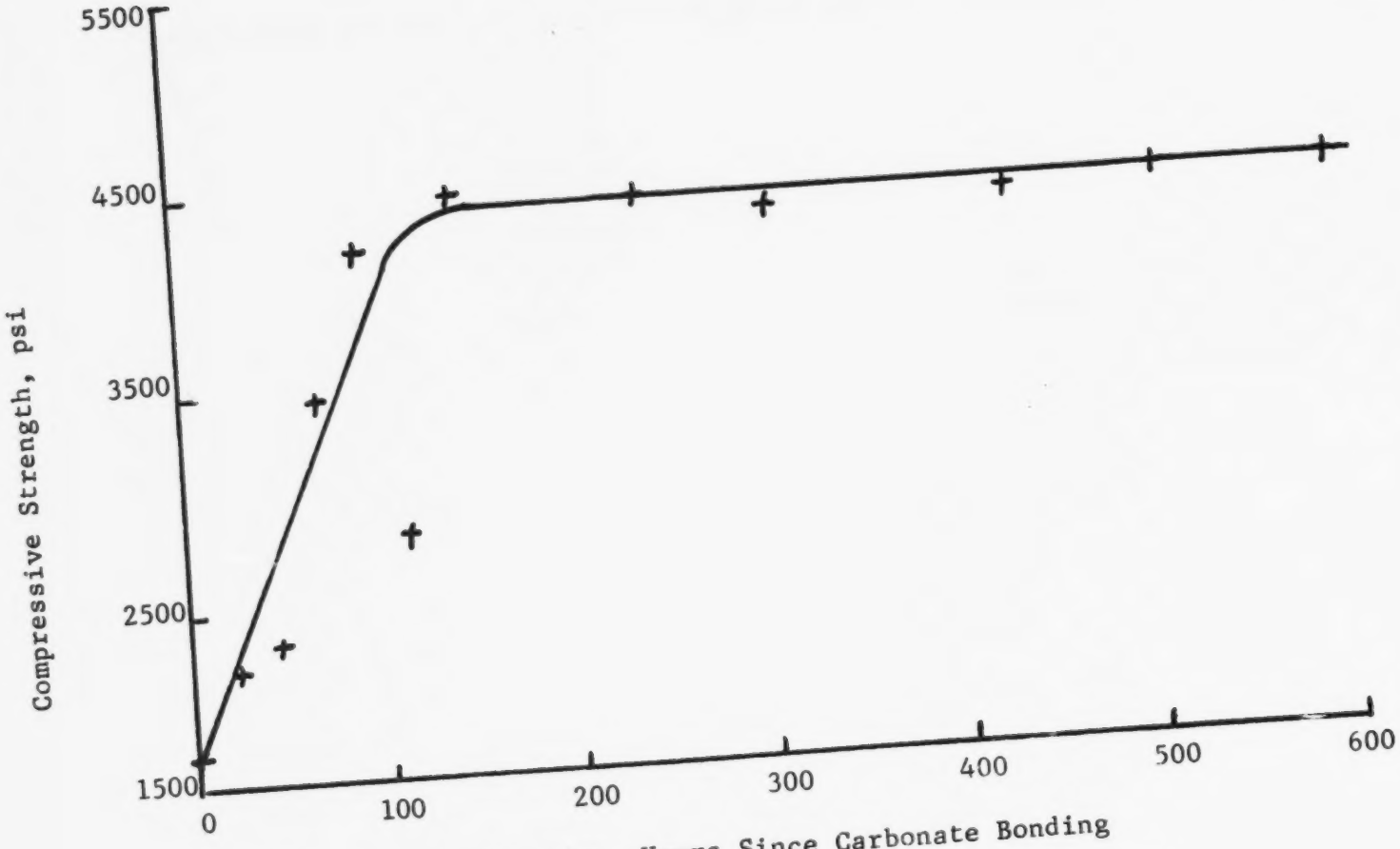


FIGURE 6-EFFECT OF CURING TIME ON COMPRESSIVE STRENGTH FOR UNBURNT BITUMINOUS COAL REFUSE

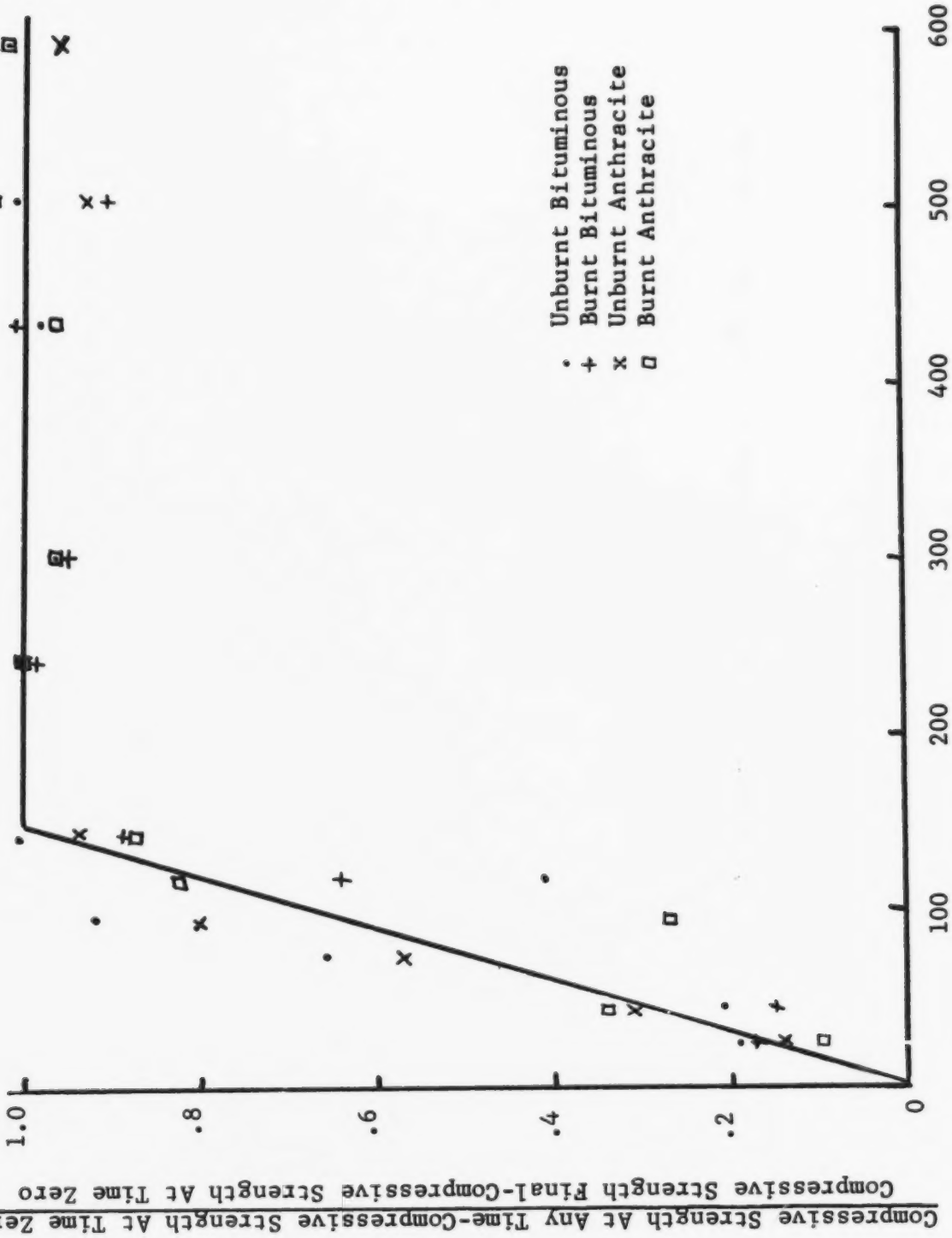


FIGURE 7-REDUCED COMPRESSIVE STRENGTH VS. CURING TIME

S_{oo} = final compressive strength at times beyond 150 hours

This figure indicates that a curing time of approximately 150 hours is required to develop the ultimate compressive strength. An investigation of this curing time phenomenon was beyond the scope of this study; however it is believed that a recrystallization of the calcium carbonate crystal matrix is occurring to yield a stronger structure. Based on this finding, compressive strength determination for all subsequent experimental investigations was performed on briquettes which were cured at least 150 hours.

Effect of Water Content on Compressive Strength

The effect of coal refuse particle size and water content on carbonate bonded compressive strength is shown in Figures 8 to 11. In these experiments the coal refuse contained 12 percent lime hydrate which was reacted with pure CO_2 for eight hours. Considering only the results for the -10 mesh material, it is seen that the maximum compressive strength results at the higher water content. Specifically, the optimum water content is 12 percent for all coal refuses except the burnt bituminous which increased to the maximum percent of water investigated (15 percent). Based on these limited results, it appears that coal refuse will be amenable to carbonate bonding at 12 to 15 percent water. The results of Figures 8 to 11 show a gradual variation in compressive strength with changes in water content. These results are encouraging since it appears that quite useable compressive strengths are obtained without resorting to unrealistic water content controls which would be a decided disadvantage to the large scale application of this process. It is also advantageous that the observed optimum water contents occur at relatively high values, because in the commercial application of the process it is more practical to add water rather than dry the coal refuse. Of course, lime rather than lime hydrate could be used if lower water content levels were required. Lime would reduce the free moisture by reacting with water to form lime hydrate.

The unburnt bituminous coal refuse exhibited a compressive strength-water content relationship which was unexpected. The compressive strength did not exhibit its usual functional dependence (i. e., increase as particle size decreases), but the optimum moisture varied in a somewhat random manner. Specifically, the optimum water content for maximum compressive strength was 12, 9, and 12 percent for the -10, -20, and -60 mesh particle size fractions respectively. These results are unusual and as yet cannot be explained.

Effect of Particle Size on Compressive Strength

Figures 8 to 11 also indicate the effect of particle size on compressive strength. Again excluding the unexplainable results for unburnt bituminous, it is seen that the compressive strength increases as the particle size of the coal refuse decreases. This is expected since a decrease in particle size (along with a wider size distribution) normally

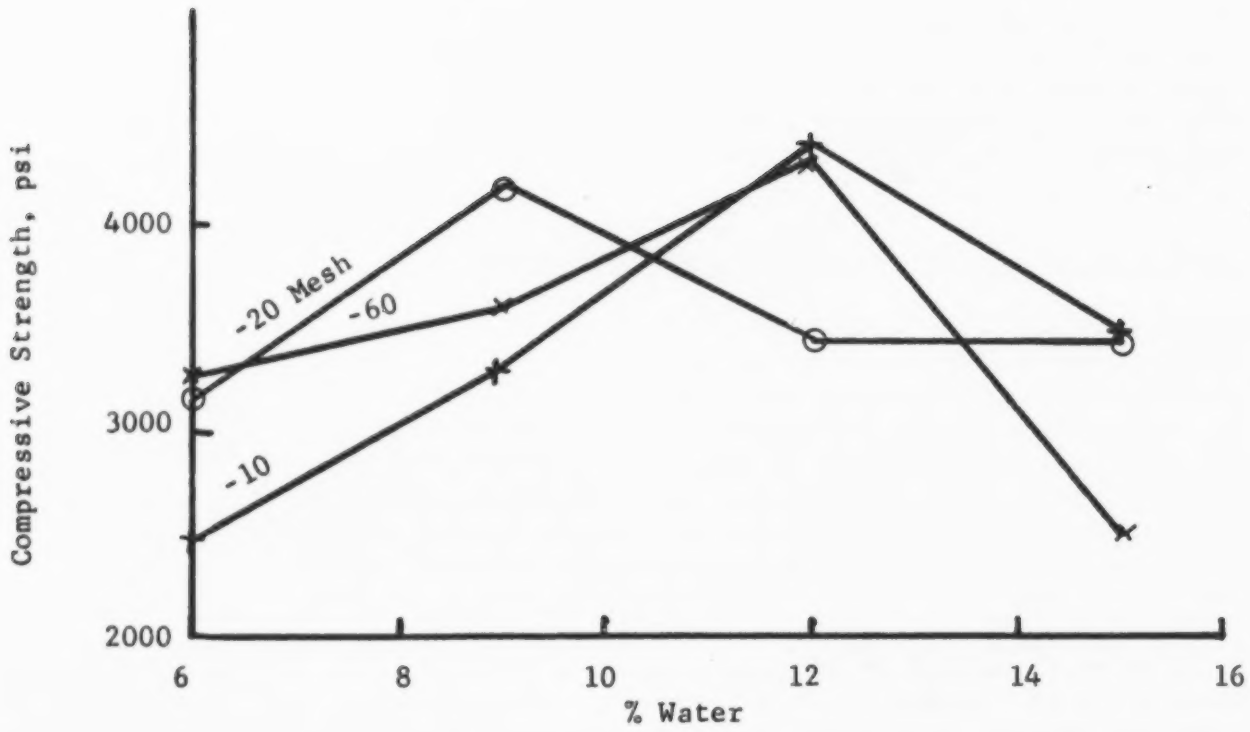


FIGURE 8-EFFECT OF PARTICLE SIZE AND WATER CONTENT ON COMPRESSIVE STRENGTH FOR UNBURNT BITUMINOUS

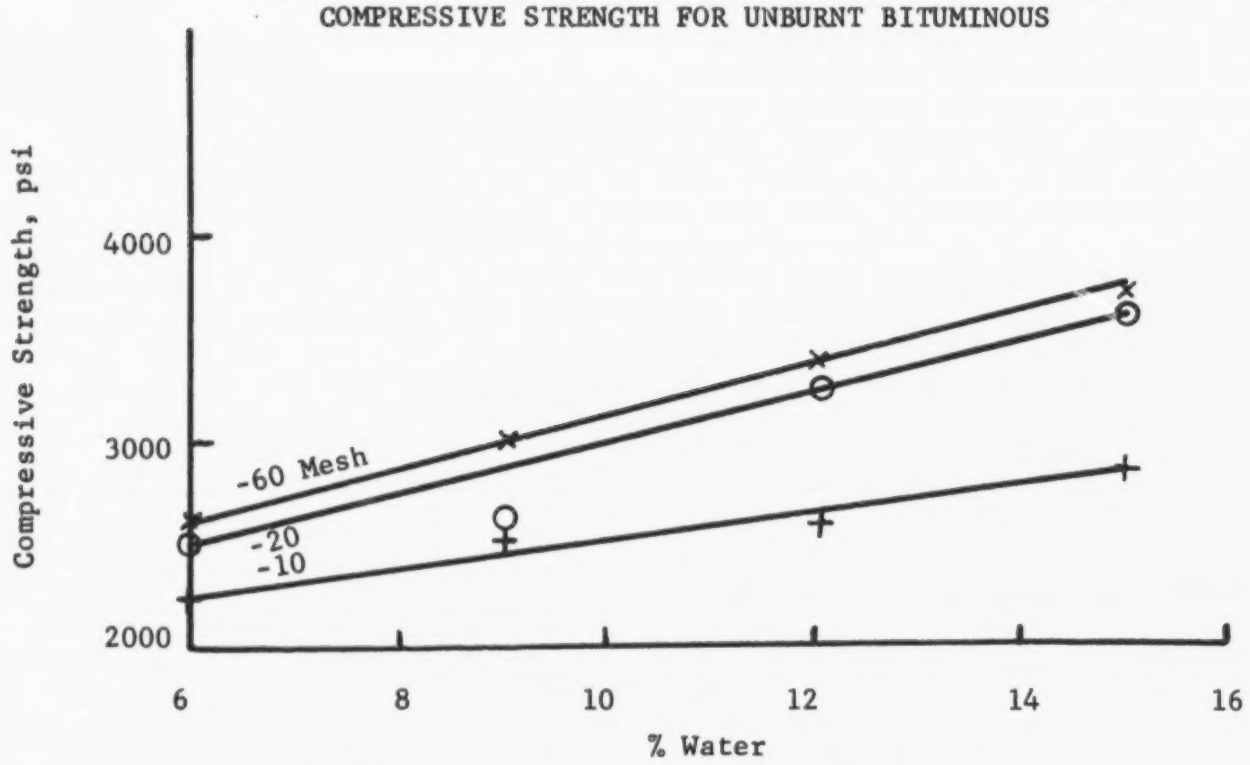


FIGURE 9-EFFECT OF PARTICLE SIZE AND WATER CONTENT ON COMPRESSIVE STRENGTH FOR BURNT BITUMINOUS

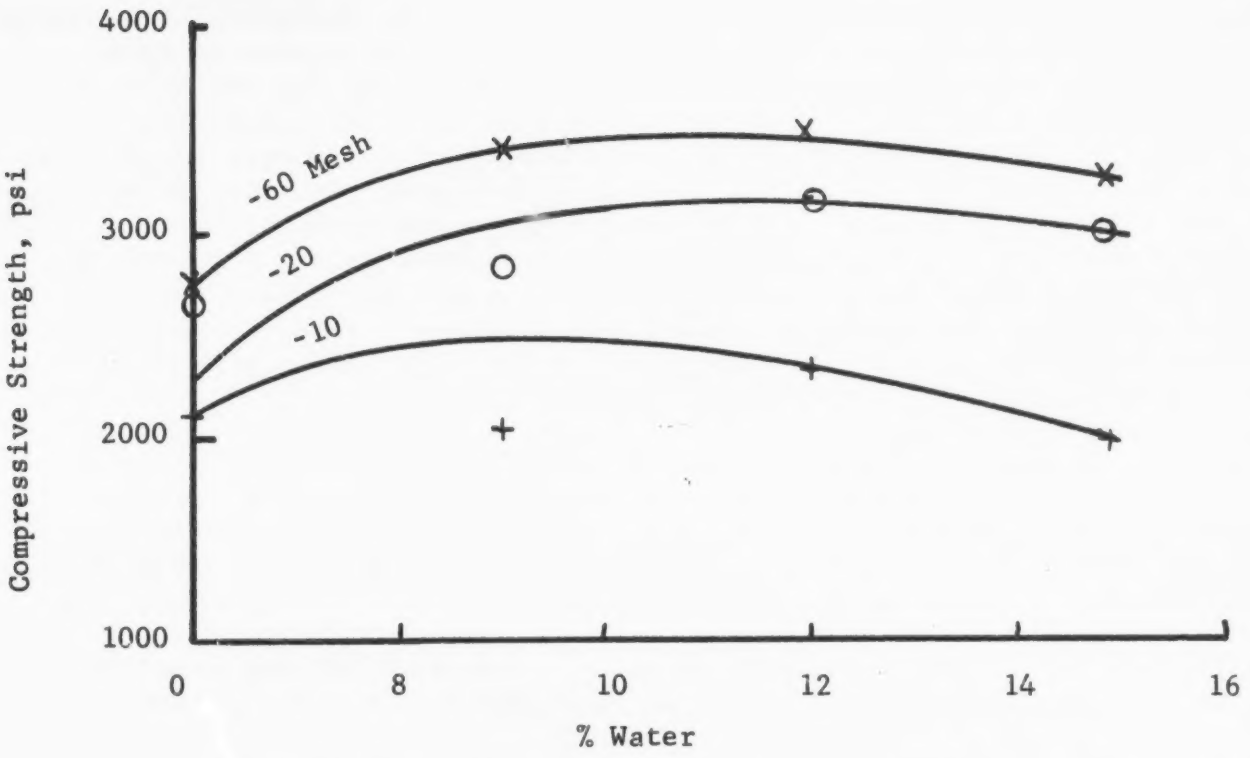


FIGURE 10-EFFECT OF PARTICLE SIZE AND WATER CONTENT ON COMPRESSIVE STRENGTH FOR UNBURNT ANTHRACITE

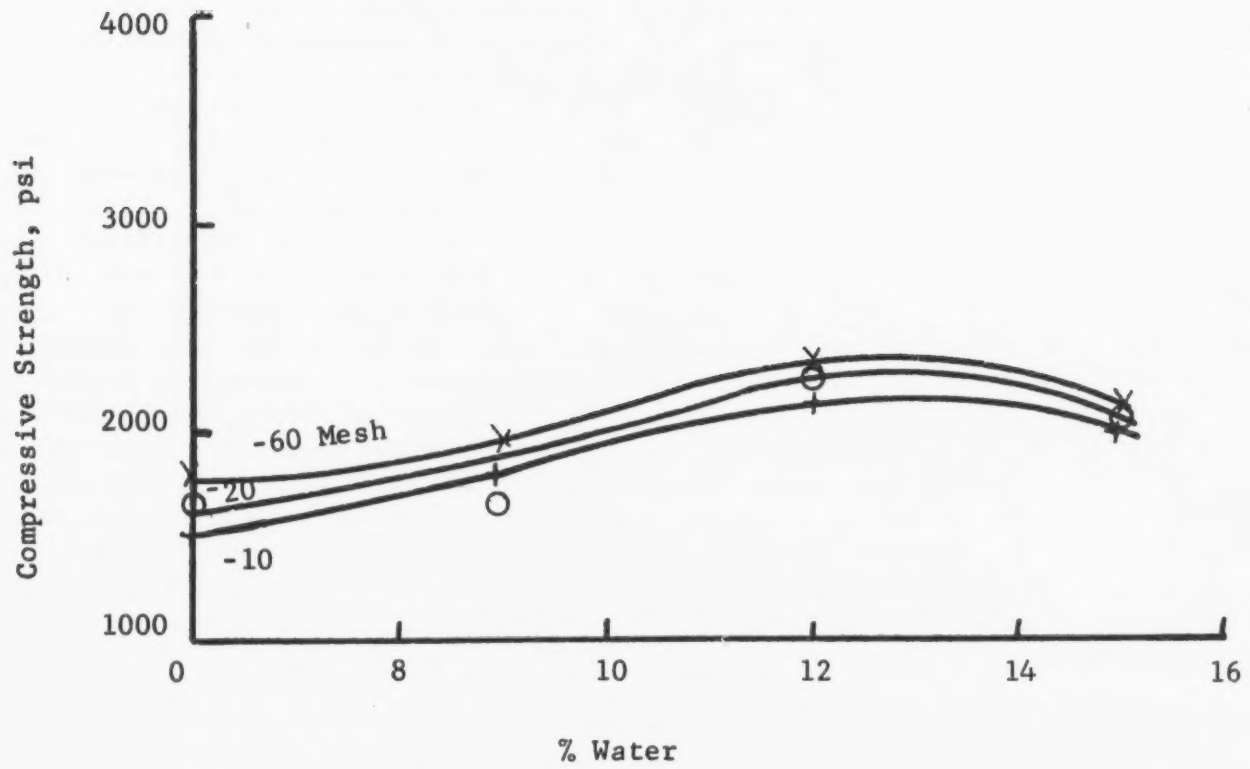


FIGURE 11-EFFECT OF PARTICLE SIZE AND WATER CONTENT ON COMPRESSIVE STRENGTH FOR BURNT ANTHRACITE

results in a more dense composite thus enhancing the formation of a strong continuous calcite crystal matrix. Additionally, the higher surface area permits more calcite-to-refuse contacts for cementing and holding the materials together. The effect of surface area on compressive strength is shown in Figure 12 where the compressive strength is plotted as a function of the specific surface area (cm^2/gram) for the -60 mesh particle size fractions of all the coal refuses except the unburnt bituminous. The carbonate bonding conditions were exactly the same as for Figures 6 and 7 and a 12 percent water content was used. Based on these findings, the smallest economically feasible particle size coal refuse should be used in the commercial application of the process to obtain maximum strength (provided the composite material is not so dense as to retard the transport of carbon dioxide into the material, and to prevent the venting of steam formed by the highly exothermic nature of the carbonate bonding reaction). If steam is prevented from rapidly exiting the carbonate bonded material, the internal pressure will build up and cause cracking with a resulting loss in strength. As explained previously, the rate of the carbonate bonding reaction can be controlled by varying the partial pressure of the carbon dioxide in the gas. The effect of carbon dioxide concentration and carbonate bonding reaction time on compressive strength will be discussed in the next section.

Effect of Carbon Dioxide Concentration and Carbonate Bonding Reaction Time on Compressive Strength

To determine the effect of carbon dioxide concentration and carbonate bonding reaction time on compressive strength, three separate experiments were conducted using a 20, 60, and 100 percent carbon dioxide gaseous mixture. Briquettes (12 percent lime hydrate, 12 percent H_2O) were removed from the reaction tubes after 2, 5, and 8 hours for each of the above gaseous mixtures. In Figures 13 to 16 are shown the results of these experiments for the -10 mesh mesh coal refuse. As is generally the rule, the compressive strength increases as the carbon dioxide concentration increases for a given carbonate bonding reaction time. This occurs because the extent of carbonation increases with carbon dioxide concentration. As seen in Figures 13 to 16, both the 60 percent and 100 percent carbon dioxide gaseous mixtures yield higher compressive strengths than the 20 percent gaseous mixture. However, for long carbonation times (less than or equal to 8 hours) compressive strengths tend to converge to a common value. This is to be expected since the ultimate strength is a strong function of the degree of carbonation. Figures 14 and 15 indicate that for burnt bituminous and unburnt anthracite the 60 percent CO_2 gaseous mixture yields a higher compressive strength than the 100 percent CO_2 gaseous mixture. This is probably caused by the carbonate bonding reaction occurring too rapidly at the higher concentration. Steam generation was too rapid causing a multitude of hair line fractures which have reduced the compressive strength.

The effect of carbonate bonding reaction time is as expected-- the compressive strength increased in each case as the time increased. More

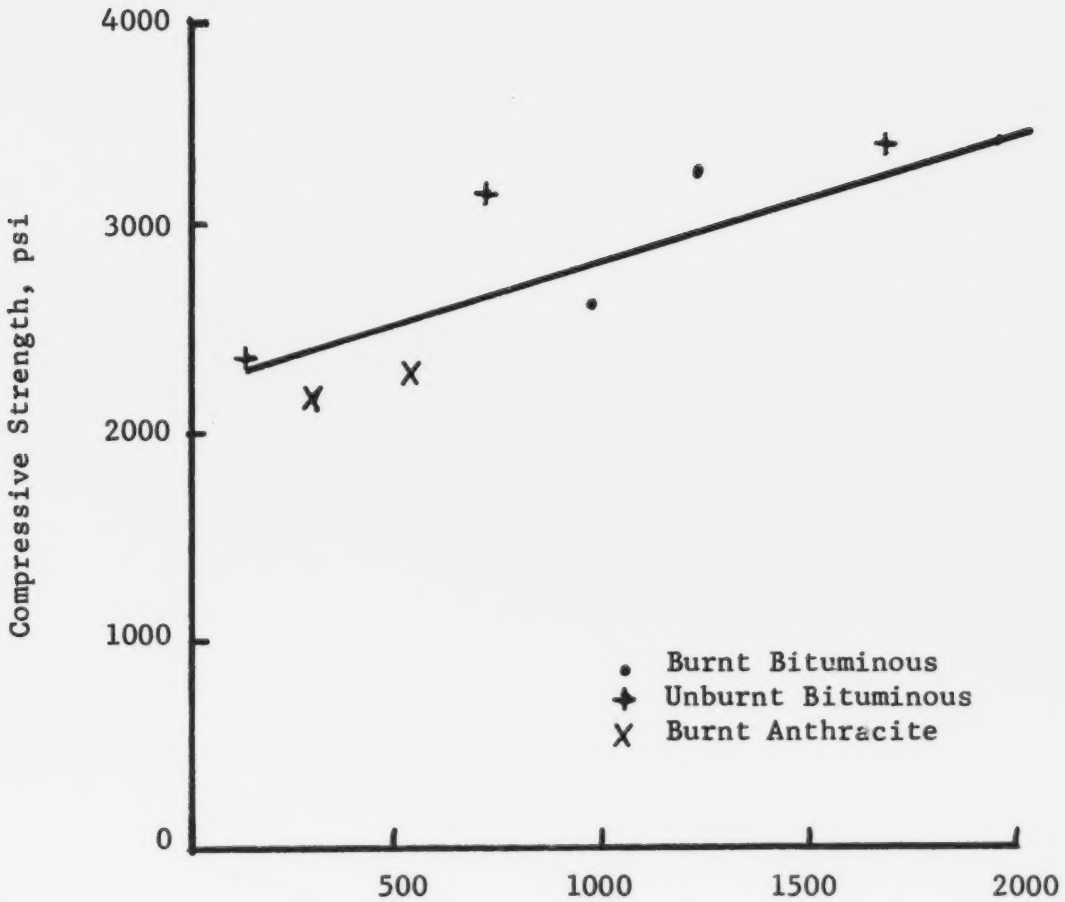


FIGURE 12-EFFECT OF SPECIFIC SURFACE AREA ON COMPRESSIVE STRENGTH

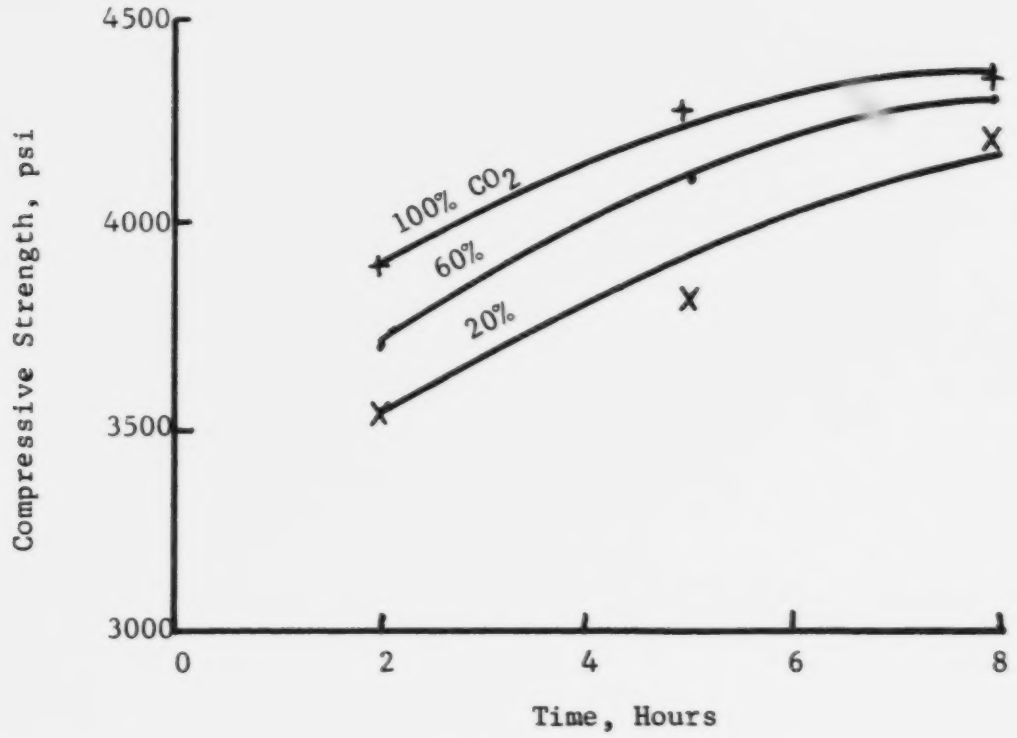


FIGURE 13-EFFECT OF CARBON DIOXIDE CONCENTRATION AND REACTION TIME ON COMPRESSIVE STRENGTH FOR UNBURNT BITUMINOUS

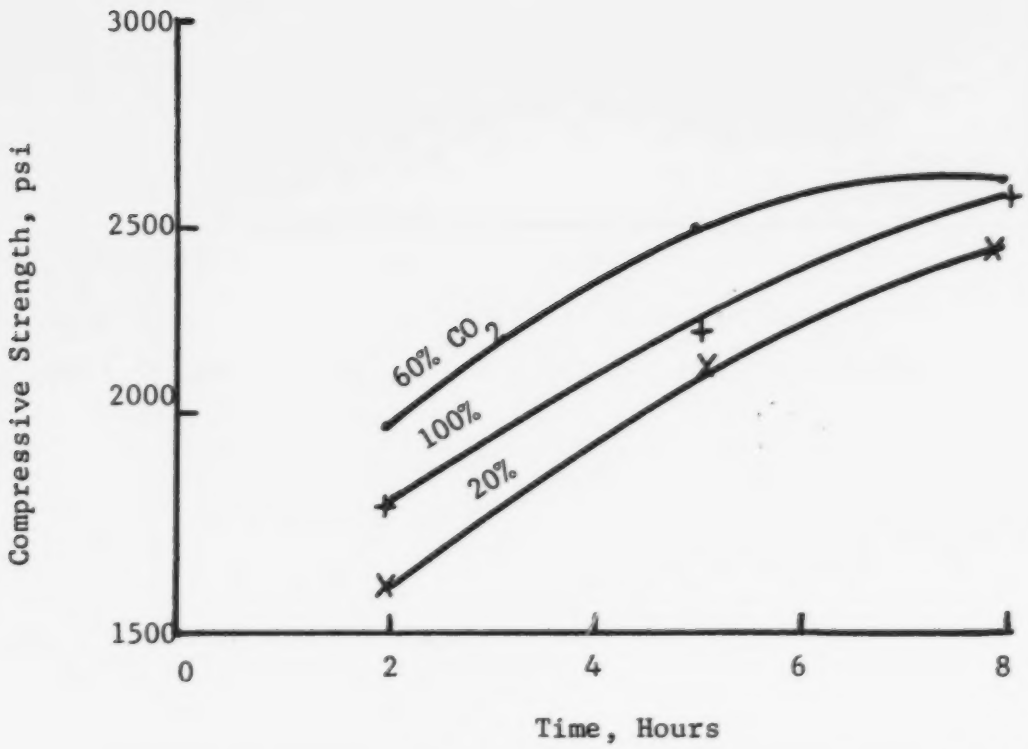


FIGURE 14-EFFECT OF CARBON DIOXIDE CONCENTRATION AND REACTION TIME ON COMPRESSIVE STRENGTH FOR BURNT BITUMINOUS

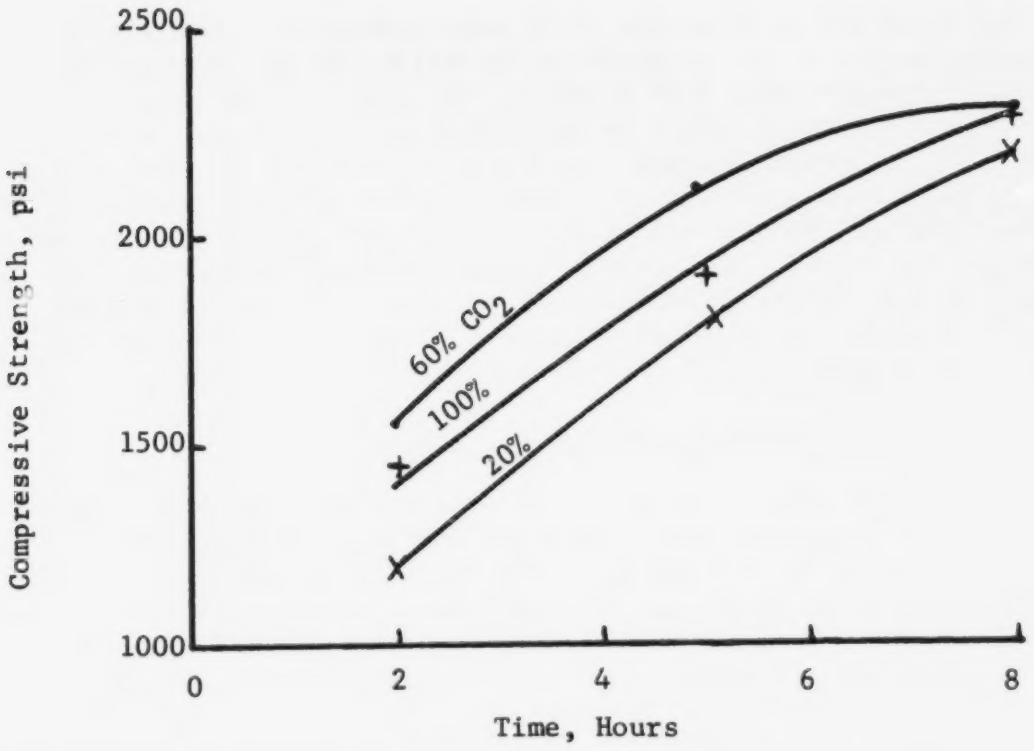


FIGURE 15-EFFECT OF CARBON DIOXIDE CONCENTRATION AND REACTION TIME ON COMPRESSIVE STRENGTH FOR UNBURNT ANTHRACITE

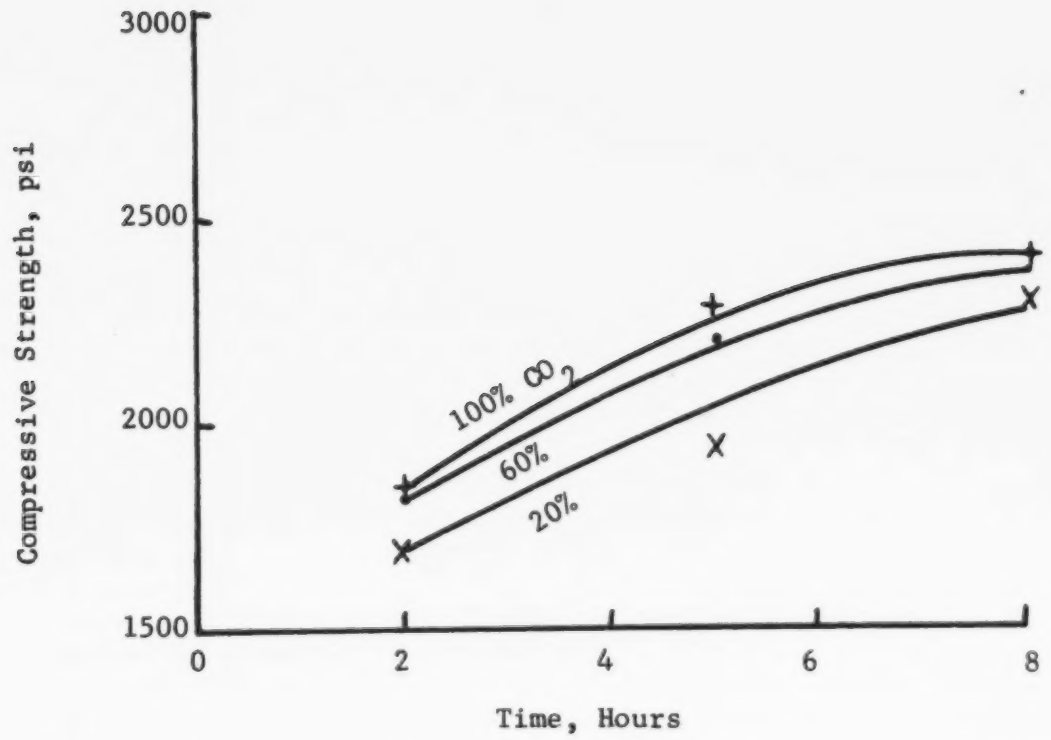


FIGURE 16-EFFECT OF CARBON DIOXIDE CONCENTRATION AND REACTION TIME ON COMPRESSIVE STRENGTH FOR BURNT ANTHRACITE

important is the observation that for an 8-hour carbonate bonding time the compressive strength is not significantly different at the various carbon dioxide concentrations. For example, the compressive strength of unburnt bituminous after 8 hours of carbonate bonding varies between 4200 and 4350 psi for carbon dioxide concentrations of 20, 60, and 100 percent. Thus, compressive strength (obtained under optimum conditions) is a strong function of the degree, or extent, of the completion of the carbonate bonding reaction. This result is encouraging because in the commercial application of the process it is economically more feasible to utilize a 20 percent carbon dioxide gaseous mixture derived from the combustion of a carbonaceous fuel rather than expensive pure CO_2.

Additional Properties of Carbonate Bonded Coal Refuse

In addition to strength, the resulting carbonate bonded coal refuse must possess other requisite properties to produce suitable construction materials. The carbonate bonded product must be able to prevent or minimize the permeation of water and air (oxygen) to inhibit acid mine water formation and must also possess a resistance to weathering. If carbonate bonded coal refuse cannot maintain its structural integrity during repeated freezing and thawing, then it cannot be an effective construction material. The properties that were investigated and presented in this section are: the air and water permeability of coal refuse and the compressive strength after repeated freeze-thaw cycles. A search of the ASTM standards did not yield an applicable standard determination for air and water permeability, therefore, special equipment and procedures were established for these determinations which were based on the commonly accepted theory of permeability. Where applicable, cement briquettes were used as a basis for comparison. These cement briquettes were prepared using one part (by weight) Portland Type One cement, 2.75 parts Ottawa Sand and ½ part water. The cement and sand were dry mixed, the water added slowly, and the wet mixture blended thoroughly. The cement briquettes were allowed to cure 28 days.

Air Permeability of Carbonate Bonded Coal Refuse

The air permeability of carbonate bonded coal refuse briquettes was determined using the apparatus schematically represented in Figure 17. The apparatus consisted of a 1¾ inch I.D. by 24 inch high plexiglass chamber on the bottom of which was cemented a coal refuse briquette. The top of the chamber was sealed with a plexiglass plate containing a pressure gauge. The air permeability was defined as the volumetric flow rate of air (ft^3/hr) per cross sectional flow area (ft^2) per unit pressure driving force ($lb/ft^2/ft$).

The chamber was pressurized with gas and the change in chamber pressure with time was measured to determine the permeability of the coal refuse briquette. Initial chamber pressures of 30, 15 and 5 psig were used. For an experimental run the chamber pressure was allowed to decrease to a pressure of 1 psig before termination. An average air permeability was then determined using the results of all the experiments.

As indicated above, the experimental procedure to determine air permeability

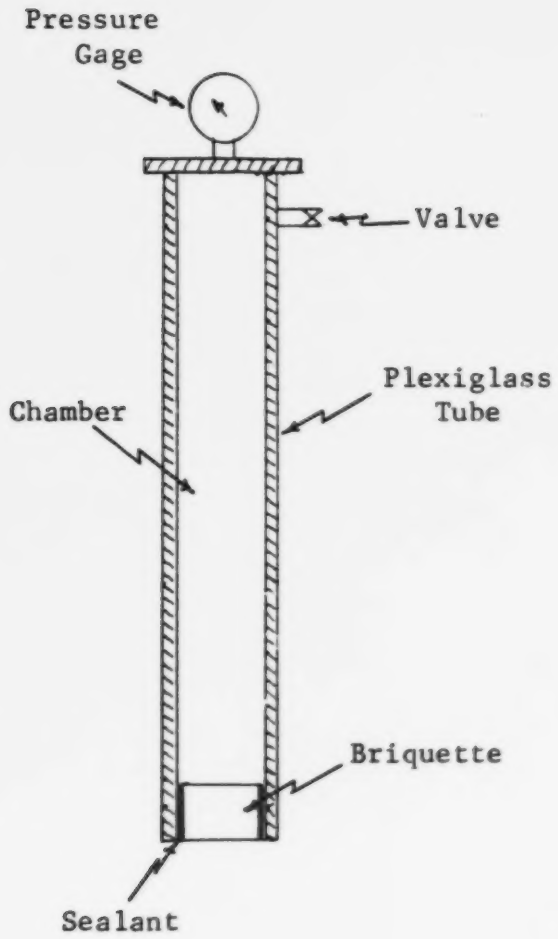


FIGURE 17-AIR PERMEABILITY APPARATUS

consisted of using a coal refuse briquette as a plug in a sealed chamber and the chamber pressure was determined as a function of time. This is an unsteady state operation in which the pressure driving force is continually changing with time. The mathematical treatment required to obtain the air permeability is somewhat involved and is presented in the Appendix.

In this experiment the air permeability for -10, -20, and -60 mesh unburnt bituminous coal refuse briquettes was determined. For comparative purposes, experiments were also run on a cement briquette of the same dimensions as the coal refuse briquettes. The results are presented in Table IV where the air permeability, the ratio of the permeability of the coal refuse briquettes to the cement briquette, and the average particle diameter of the coal refuse (determined from the screen analysis presented in Table I) are presented.

TABLE IV

Air Permeability of -10, -20, & -60 Mesh
Unburnt Bituminous Coal Refuse

Sample	Air* Permeability	Permeability of Coal Refuse/ Permeability of Cement	Average Particle** Diameter
Unburnt Bituminous -10 Mesh	2.7×10^{-4}	9	.046
Unburnt Bituminous -20 Mesh	6.0×10^{-5}	2	.013
Unburnt Bituminous -60 Mesh	2.4×10^{-5}	0.8	.008
Cement	3.0×10^{-5}		

* $ft^3/(hr - ft^2 - (lb - ft^2/ft))$

** Diameter in centimeters

It is seen for the -10 mesh briquettes that the permeability ratio is 9 times that of the cement briquette whereas the ratio is 2 and 0.8 for the -20 and -60 mesh coal refuse. This infers that the smaller particle size fractions (-20 mesh or lower) carbonate bonded coal refuse compare quite well with cement and would provide an adequate seal against air permeation. In order to make the air permeability results generally applicable to all types of coal refuses, Figure 18 was prepared. Figure 18 is a plot of the air permeability for unburnt bituminous coal refuse vs. the average particle diameter and can be used to estimate the permeability of a coal refuse provided the particle size distribution is known.

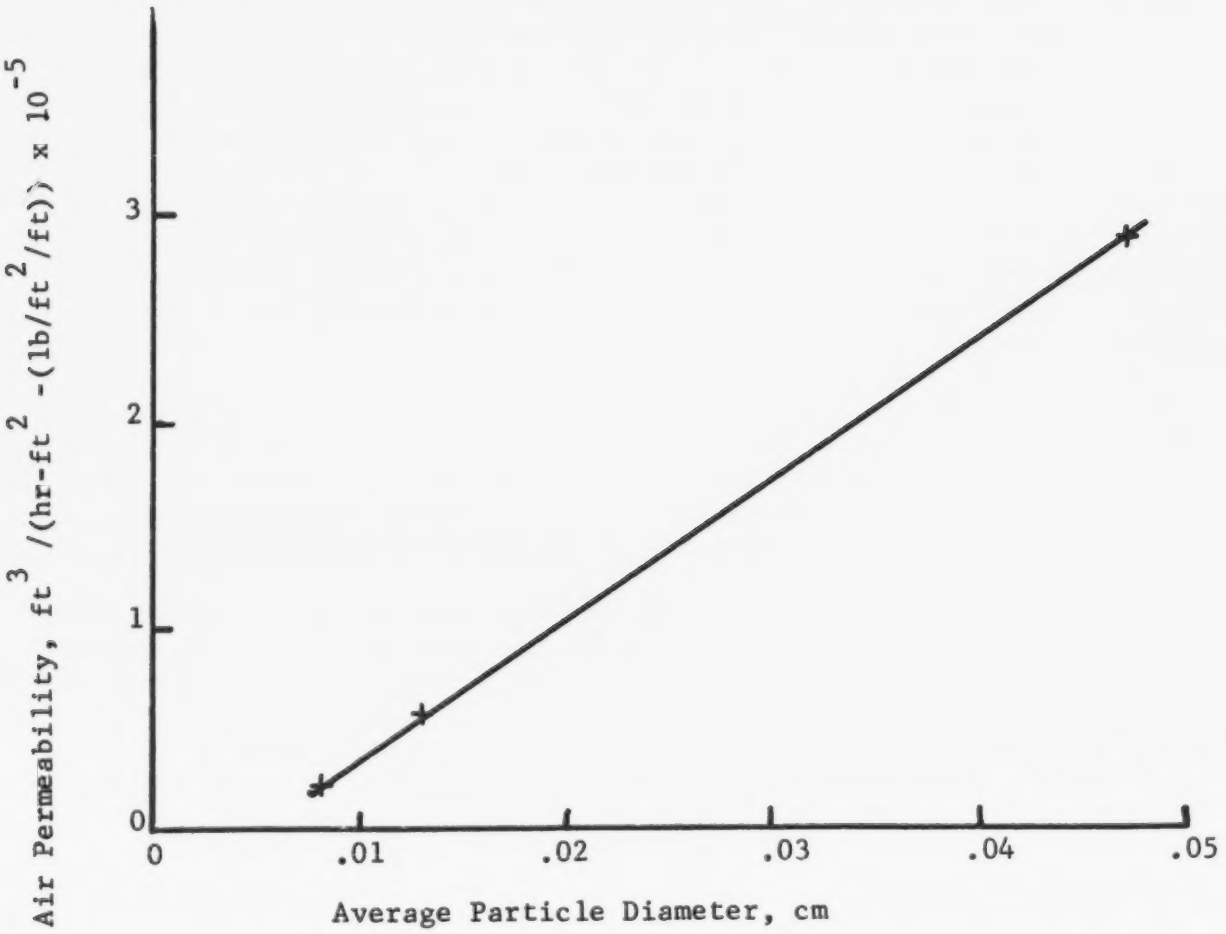


FIGURE 18-AIR PERMEABILITY VS. AVERAGE PARTICLE DIAMETER

Water Permeability of Carbonate Bonded Coal Refuse

The water permeability of coal refuse was determined in much the same manner as air permeability. The apparatus for the water permeability determination is shown in Figure 19, and consists of a 1¼ inch I.D. by 24 inch high plexi-glass primary chamber sealed on top with a plexi-glass plate containing a valve and on the bottom with a coal refuse briquette. For this test, an additional chamber is attached to the primary chamber and located beneath the briquette to collect the water permeating through the briquette and to prevent unrealistic permeation rates due to convective air flows about the exposed surface of the briquette. In addition, water permeating through carbonate bonded coal refuse will probably enter into surroundings which will normally be saturated with water vapor. The lower chamber, therefore, provides a water vapor saturated atmosphere to better simulate actual conditions and provide more meaningful results. The lower chamber contains a small hole on its side to vent evaporated water and prevent a build up of pressure.

The water permeability test was conducted by initially filling the primary chamber with water to a level of 20 inches and, on a daily basis measuring the amount of water lost due to permeation. After the quantity of water loss was determined, this amount was added back into the primary chamber to maintain a constant pressure driving force.

This test was run for 14 days and an average rate of water permeation determined. For all practical purposes this test was run on a steady state basis in which the water pressure driving force was constant; consequently, the water permeability of coal refuse can be directly calculated since the flow area of the briquette, the thickness of the briquette, the constant water pressure driving force, and the average rate of water permeation are known.

The water permeability of -10, -20, and -60 mesh unburnt bituminous coal refuse and a cement briquette is shown in Table V.

TABLE V

Water Permeability of Coal Refuse

Sample	Permeability*	Permeability Ratio**
Unburnt Bituminous, -10 Mesh	5.5×10^{-9}	4.0
Unburnt Bituminous, -20 Mesh	2.5×10^{-9}	1.8
Unburnt Bituminous, -60 Mesh	2.5×10^{-9}	1.8
Cement	1.3×10^{-9}	

* Water Permeability in lbs/(hr. - ft.^{2} - (lbs./ft.^{2}/ft.))

** Permeability of Coal Refuse/Permeability of Cement

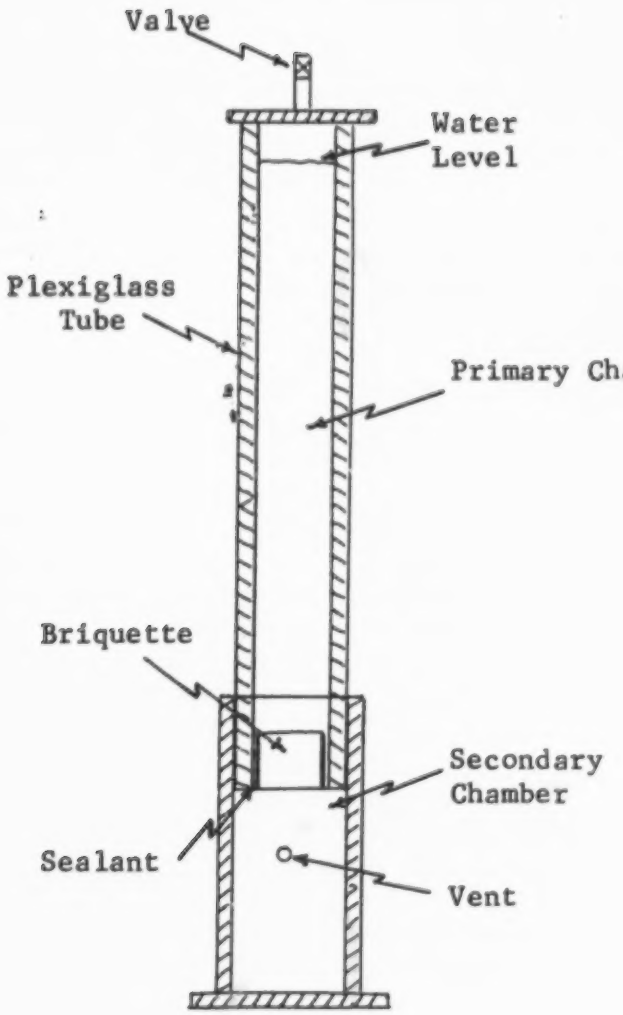


FIGURE 19-WATER PERMEABILITY APPARATUS

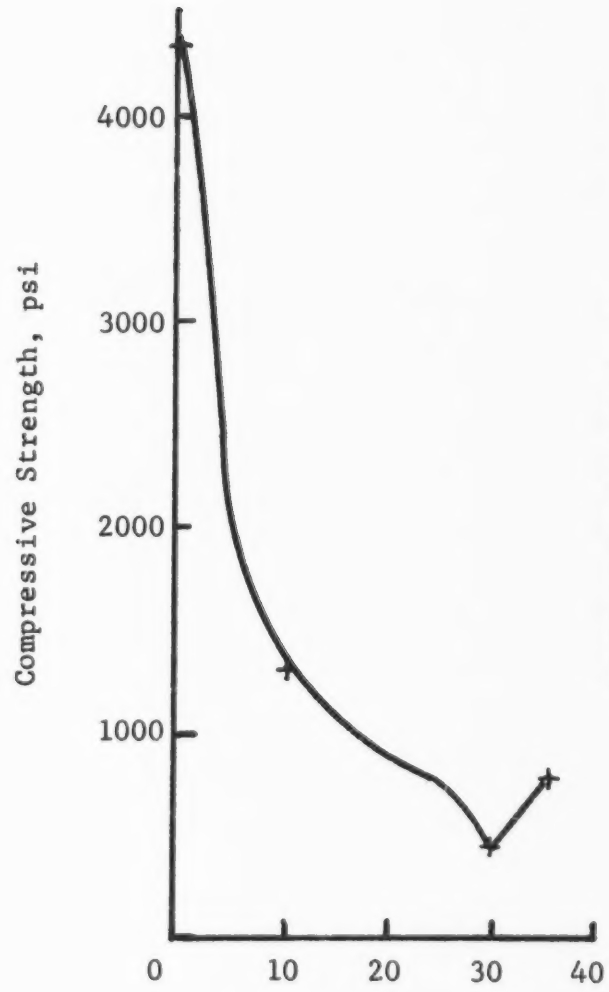
Water permeability is the mass flow rate of water per crossectional flow area per unit pressure driving force. Also shown in Table V is the water permeability ratio defined as water permeability of coal refuse divided by the water permeability of cement. It is interesting to note that carbonate bonded coal refuse compares quite well with cement in prevention of water permeation. This is particularly so at the lower particle size fractions of -20 and -60 mesh where the permeability ratio is 1.8. Results indicate that carbonate bonded coal refuse would provide an adequate seal against water permeation and minimize acid mine water formation.

Freeze-Thaw Test on Carbonate Bonded Coal Refuse

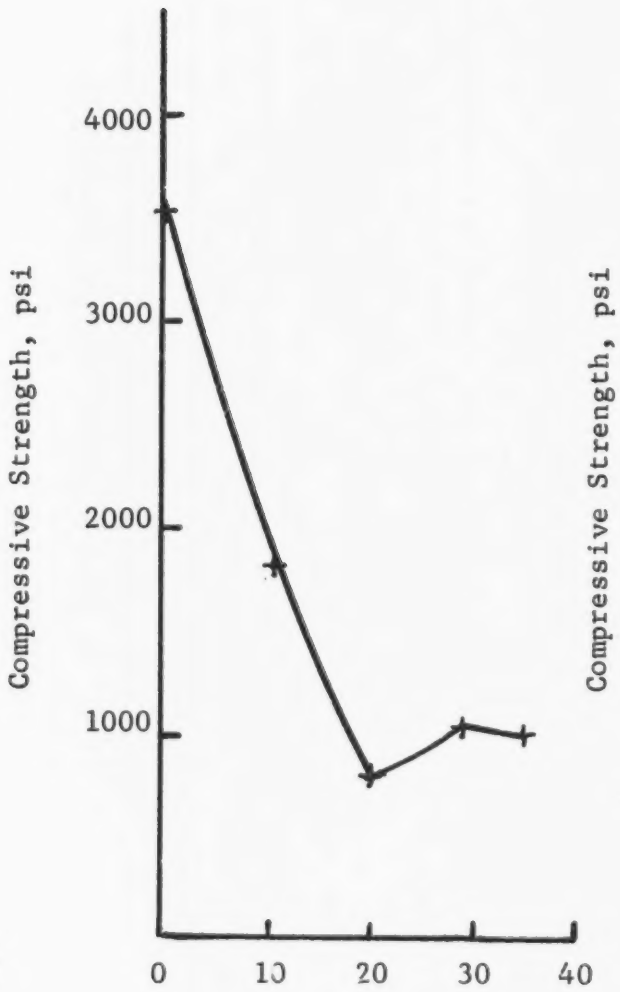
Freeze-thaw tests were performed on a series of -10, -20, and -60 mesh unburnt bituminous coal refuse briquettes. The freeze-thaw test was based on the ASTM designation; C290-67 entitled, "Standard Method of Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water". The freeze-thaw test, as modified for this study, is presented in the Appendix. The objective of this test was to determine compressive strength of coal refuse briquettes as a function of the number of freeze-thaw cycles to which they had been subjected. Figures 20 to 22 present the briquette compressive strength as a function of the number of freeze-thaw cycles for -10, -20, and -60 mesh unburnt bituminous coal refuse. The compressive strength in the 20 to 35 freeze-thaw cycle range tends to stabilize at a relatively constant value of 700 to 900 psi for each of the particle size fractions.

It must be noted that subjecting a composite material of small dimensions (1-1/8 inch diameter by 1 inch high briquettes) to 35 freeze-thaw cycles is an extreme test. The ASTM standard test method contemplates the use of specimens not less than 3 inches nor more than 5 inches in width and depth and not less than 14 inches nor more than 16 inches in length. The normal erosion of surface edges which occurs during freeze-thaw testing does not seriously effect large specimens, whereas for small briquettes the effect on strength is quite dramatic as evidenced by the results of this study. An examination of the coal refuse briquettes after 35 cycles revealed an erosion of about ¼ inch of material almost completely around all edges. This reduced the area on which the compressive strength test load was applied causing the briquette to fail at lower loads and indicate a lower compressive strength based on the original one square inch area. For comparison, cement briquettes were also subjected to freeze-thaw testing. The cement briquettes had an initial compressive strength of 2000 psi which reduced to 1200 psi after 35 freeze-thaw cycles. An examination of the cement briquettes after 35 cycles revealed an erosion of about 1/8 inch of material almost completely around all edges.

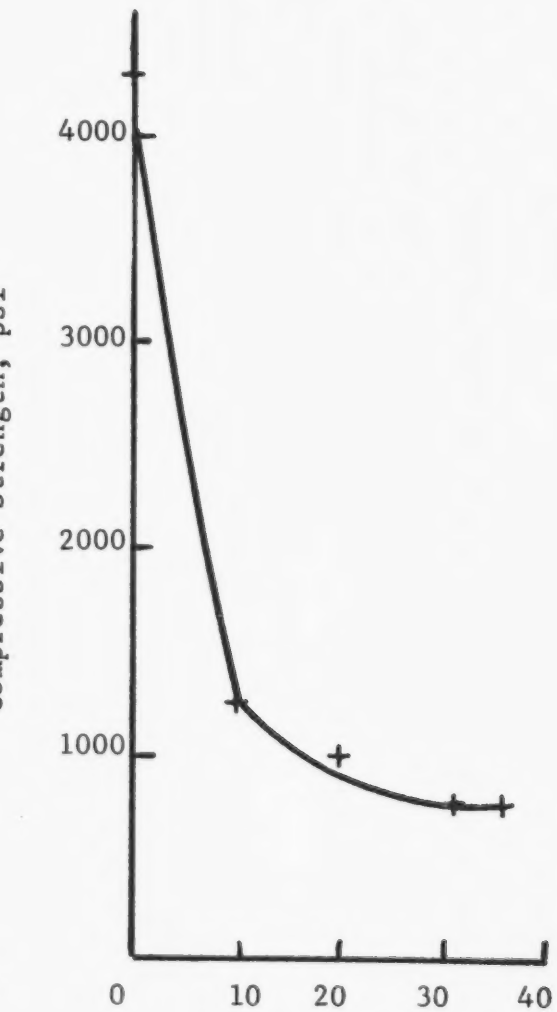
Even under extremely unfavorable test conditions, the carbonate bonded coal refuse yielded compressive strengths in the order of 700-900 psi. Consequently, it should adequately withstand the effects of severe



Freeze-Thaw Cycles
(--10 Mesh)
FIGURE 20



Freeze-Thaw Cycles
(--20 Mesh)
FIGURE 21



Freeze-Thaw Cycles
(--60 Mesh)
FIGURE 22

EFFECT OF FREEZE-THAW CYCLES ON COMPRESSIVE STRENGTH FOR UNBURNT BITUMINOUS COAL REFUSE

changes in temperature.

Suggested Operating Parameters for Carbonate Bonding Process

The economics of coal refuse carbonate bonding depend primarily on four controllable factors: the particle size of the coal refuse, quantity of lime hydrate required, carbon dioxide concentration and time of carbonation.

In the present study, particle size effects were evaluated over a rather narrow range limited by the size of the briquette die employed. However, based on the results obtained, it is reasonable to expect that the carbonate bonding process for the conversion of coal refuse to paving materials will accommodate fill material containing a top size of one inch. To maintain air and water permeability conditions as developed in this report, it will only be necessary to specify a particle size distribution so that minimum porosity (i.e., maximum density) will be achieved. Data are available in literature that will permit an estimate of the proper size consist to use in commercial applications.

Depending upon strength criteria established for commercial applications, this study has shown that a maximum of 12 percent lime hydrate will yield compressive strengths approaching 4400 psi for coal refuse. Should lower compressive strength be acceptable, the amount of lime hydrate can be decreased accordingly.

It has been found that adequate carbonate bonded coal refuse strengths have been obtained when a 20 percent carbon dioxide gaseous mixture is used for reaction times of 8 hours. Assuming that faster set times are not required, a simple inexpensive carbon dioxide gas generator can be used to yield carbon dioxide concentrations of about 15 to 20 percent. Faster set times will require the use of carbon dioxide generators producing a higher purity gas.

When using coal refuse material, the data indicate that a moisture content of about 9 to 15 percent will be required to obtain optimum strength. This moisture requirement can readily be realized at the site.

APPLICATIONS OF CARBONATE BONDED COAL REFUSE

The primary objective of this study was to determine the feasibility of utilizing coal refuse as a fill material in the carbonate bonding process. The results of this study show that carbonate bonded coal refuse has the necessary strength properties for construction applications and the necessary sealant properties to effectively prevent the permeation of air and water which cause the generation of acid constituents in water. The applications of carbonate bonded coal refuse are numerous. The carbonate bonded process utilizing coal refuse could be employed to (1) construct secondary roads utilizing the formed carbonate coal refuse as is, (2) provide a strong inexpensive base material for major road construction, (3) provide a first class road when used in conjunction with a thin layer of tar or similar material, (4) provide a strong inexpensive sealant layer on existing coal refuse piles, and (5) make bricks. These applications, except (4) above, have the advantage that coal refuse can be worked off thus eliminating unsightly coal refuse piles. Also the current production of coal refuse could be utilized in the process to prevent the formation of new or the enlargement of old coal refuse piles.

Although no work has been completed on the field testing of the carbonate bonding process employing coal refuse or spoil bank material, the bench scale study and earlier experimentation (on a 4 foot square patch of carbonate bonded soil) show that the following proposed commercial concept is feasible for both sealing coal refuse piles and constructing roads. The coal refuse or spoil bank material is tilled to a predetermined depth, depending on the particular application. During the tilling operating, lime hydrate and water (if necessary) in the proper proportions, are introduced into the tilled material. The tilling action not only loosens the fill, but is also effective for blending and making a homogeneous mixture of lime and fill material. Once the tilling and blending step has been completed, perforated plastic pipe is placed on four foot centers underneath the surface of the blended material. The perforated plastic pipe is expendable and remains in place under the carbonate bonded material. The plastic pipe is connected to a portable carbon dioxide generator which can be a burner for coal refuse, coal, oil, or any other carbonaceous fuel which generates products of combustion containing carbon dioxide. Once the plastic pipe is in place and connected to the generator, the blended material is then tamped down by means of a roller. The flue gases are pumped under pressure (approximately five pounds per square inch) into the perforated plastic pipe. At this time the portable carbon dioxide generator is started and gaseous carbon dioxide along with the inert components of the flue gas are pumped into the perforated pipe. As the carbon dioxide permeates upward through the lime hydrate-fill material mixture, the carbonate bonding reaction starts and hardens the blend. The conversion of the lime hydrate to the carbonate form occurs with the visible evolution of steam. When the steam has stopped emanating from the pavement, the reaction is completed and the spoil bank or coal refuse material will be surfaced hardened with a

concrete-like covering. At present the effect of the combustion products other than carbon dioxide on the carbonate bonding reaction is not known. Since these gases will consist mainly of nitrogen, unburnt oxygen and water vapor, it is anticipated that there will be little or no effect. If future work indicates that the water vapor decreases the carbonation reaction rate, the initial water content of the coal refuse may be adjusted to compensate for the water contained in the flue gas.

As is evident from the foregoing description, the process is relatively simple using existing road grading equipment, requires no unusual equipment or highly skilled labor, and uses locally available materials (with the exception of the lime hydrate) thus minimizing material handling.

To carry out the process, the following items of equipment will be required

1. A portable carbon dioxide generator

2. Expendable perforated plastic pipe

3. Earth moving and compacting equipment

4. A roto-tiller attachment for tractors

The earth moving and compacting equipment are not unique to the carbonate bonding process and are considered part of the normal inventory of maintenance construction equipment. If the work is carried out as outlined above, a rotary tiller attachment to the tractor will be needed. Such a tilling attachment is readily available as a stock item.

The portable carbon dioxide generator is also readily fabricated. The equipment will essentially consist of a burner and a blower. The burner which can operate on a convenient fuel (coal, coal refuse, bottled gas, fuel oil, or other carbonaceous fuels) would generate products of combustion containing 15 to 20 percent carbon dioxide. These flue gases will be compressed to about five pounds per square inch for introduction into the perforated plastic pipe. If rapid setting of the carbonate bonded material is required, concentrated carbon dioxide can be generated by the addition of an amine absorber to the above equipment. Economics will dictate the type of carbon dioxide generator.

Cost for using carbonate bonding as a method for sealing coal refuse piles is difficult to establish, because full scale paving tests have not been completed. However, by assuming that labor costs for carbonate bonding are comparable to paving techniques which require similar operations, an approximate cost estimate can be made.

Results of a survey of construction costs associated with other paving methods are presented in Table VI, which shows paving costs as a function

of construction material and depth of paving. If it is assumed that carbonate bonding labor costs are comparable to those for asphalt, the data on Table VI for 2-inch asphalt on 4-inch subbase indicate that the labor costs for a 6-inch carbonate bonded pavement will be $0.85 per square yard. Assuming labor cost varies linearly with the

TABLE VI

Paving Costs of Various Materials*

Construction Material	Total Cost	Labor Cost	Material Cost
4-inch thick concrete on 6-inch subbase	$7.87/sq. yard	$5.00/sq. yard	$2.87/sq. yard
2-inch asphalt on existing base	3.12/sq. yard	0.56/sq. yard	2.56/sq. yard
2-inch asphalt on 4- inch subbase	4.68/sq. yard	0.85/sq. yard	3.83/sq. yard
3-inch asphalt on 12-inch subbase	7.62/sq. yard	1.37/sq. yard	6.25/sq. yard
4-foot layer of dirt	1.33/sq. yard	1.33/sq. yard	No Cost
1-½ foot layer of dirt	0.68/sq. yard	0.68/sq. yard	No Cost

thickness of the seal over the range of 6 to 15 inches, labor costs for the carbonate bonded process as a function of thickness were calculated and are presented in Table VII.

TABLE VII

Paving Costs for the Carbonate Bonding Process

Thickness	Total Cost	Labor Cost	Material Cost
2 inches	$0.83/sq. yd.	$0.63/sq. yd.	$0.20/sq. yd.
4 inches	1.05/sq. yd.	.74/sq. yd.	0.31/sq. yd.
6 inches	1.28/sq. yd.	.85/sq. yd.	0.43/sq. yd.
8 inches	1.60/sq. yd.	.97/sq. yd.	0.63/sq. yd.
10 inches	1.82/sq. yd.	1.08/sq. yd.	0.74/sq. yd.
12 inches	2.05/sq. yd.	1.10/sq. yd.	0.95/sq. yd.
15 inches	2.48/sq. yd.	1.37/sq. yd.	1.11/sq. yd.

*Popper, H, "Modern Cost Estimating Techniques", McGraw-Hill Co., New York, p. 101 (1970), except cost of dirt which was obtained by private communication.

Because it is possible to substitute equipment costs for labor costs, and vice versa, labor and equipment costs are combined in Table VII under the heading "Labor Cost". The "Labor Cost" also includes the cost of earth tilling, labor and equipment required to crush coal refuse to a particle size distribution suitable for carbonate bonding.

Material cost for carbonate bonding as a function of seal or paving thickness is also presented in Table VII. In the material cost calculations it was assumed that coal refuse is available on site at no cost and is used as fill and as fuel to produce the carbon dioxide required in the process. Lime hydrate was assumed to cost $25 per ton delivered and 12 percent lime hydrate was assumed to be used in the fill.

Perforated hose, used to distribute the carbon dioxide in the material to be carbonate bonded was assumed to be located on four-foot centers in the pavement. For carbonate bonded material thicknesses of more than 6 inches, additional hose was assumed. Pending establishment of specifications, the retail price of perforated hose, $0.04 per linear foot was assumed. Using these cost data, the total cost (material and labor) of carbonate bonding was calculated for various sealing or paving thicknesses and is presented in Table VII.

For sealing of coal refuse piles, it is believed that a 6-inch thick carbonate bonded layer will have air and water permeability and load bearing characteristics comparable to a 4 foot layer of dirt. A comparison of Tables VI and VII indicates that the total cost per square yard of seal is slightly lower for the carbonate bonding process. Sealing with the four foot layer of dirt costs $1.33 per square yard whereas a 6-inch thick carbonate bonded seal costs $1.28 per square yard. Since the costs were conservatively estimated, it would appear that carbonate bonding offers considerable economic superiority for sealing coal refuse piles.

At present, the State of Pennsylvania requires that a 1½ foot layer of dirt be used to seal a coal refuse pile. The cost of a 1½ foot layer of dirt is estimated to be $0.68 per square yard (Table VI) compared to a cost of $0.83 per square yard for a 2-inch carbonate bonded layer (Table VII). A 2-inch layer of carbonate bonded coal refuse is of a much more permenant nature and will be far superior to a 1½ foot layer of dirt as concerns air and water permeability and load bearing characteristics. Consequently, it is believed that the $0.15 difference in cost per square yard is a necessary additional cost to insure the prevention of acid water formation.

If carbonate bonded coal refuse is used to construct a secondary road then its cost should be compared with a 2-inch asphalt layer on a 4-inch subbase (4.68 per square yard-Table VI). For a 6-inch carbonate bonded layer, the cost is $1.28 per square yard (Table VII). These results indicate that for secondary road building applications carbonate bonding costs considerably less than asphalt paving.

Cost of carbonate bonded coal refuse used as a strong base material for road building can be compared to the cost of other materials from data presented in Table VI. From Table VI, it is seen that a difference of $1.56 ($4.68-$3.12) per square yard exists for a 2-inch asphalt paving with and without a 4-inch subbase. The $1.56 difference represents the cost of the subbase. A 4-inch subbase of carbonate bonded coal refuse would cost $1.05 per square yard (Table VII). As is evident, carbonate bonded coal refuse is significantly less expensive than conventional subbase materials. If 12-inch thick carbonate bonded coal refuse is covered with a 2-inch layer of asphalt to provide a first-class road, its cost should be compared to alternatives of either 4-inch concrete on 6-inch subbase or 3-inch asphalt on 12-inch subbase. For a 2-inch asphalt layer on a 12-inch carbonated bonded subbase, the cost of asphalt will be $3.12 per square yard (Table VI) and the cost of the carbonate bonded subbase will be $2.05 per square yard (Table VII). Thus the cost of such a first-class road is $5.17 per square yard, which is significantly less than $7.87 and $7.62 per yard for the concrete and asphalt alternatives, respectively (Table VI).

In summary, the above indicates that substantial economics can be realized if the carbonate bonding process is utilized as a refuse pile sealant or road construction technique. This should induce coal producers to cover or utilize their coal refuse, thereby minimizing the formation of acid water.

We suggest the process be demonstrated by actually sealing a coal refuse pile to prevent acid water formation. This would also allow development of large scale construction techniques necessary to apply the process. Based on results of this demonstration, an engineering evaluation will be made, construction standards and procedures developed, and costs established for future application of the process.

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APPENDICES

Determination of Air Permeability

When a pressure difference exists across a porous solid, a flow of gas through the solid will occur. This is not diffusional flow in the usual sense but it can be described using the methods of diffusion. For the permeation of gas through a coal refuse briquette, where the diameter of the capillaries is small and the gas velocity through the solid is small, flow will be streamline and can be described by Poiseuille's law for a compressible fluid obeying the perfect gas law

$$N = \frac{d^2 g}{32 u l R T} P_a (P_1 - P_2) \qquad (1)$$

where $P_a = (P_1 + P_2)/2$. A table of nomenclature is presented in Table VIII for the following discussion.

TABLE VIII

Table of Nomenclature for Air Permeability

A	Area through which gas is flowing, ft^2
d	Diameter of a capillary, ft
g	Conversion factor, 4.17×10^8 lb. mass - ft/(lb. force - hr.)^2
l	Length of capillary, ft
N	Rate of diffusion, lb. moles/hr. - ft.^{2}
n	Moles, lb. moles
P	Pressure, lb./ft^2 (abs.)
P_1	Gas pressure in pressure vessel, lb./ft^2 (abs.)
P_2	Atmospheric pressure, lb./ft^2 (abs.)
P_o	Gas pressure in pressure vessel at time zero, lb./ft^2 (abs.)
P_a	$(P_1 + P_2)/2$, lb./ft^2 (abs.)
R	Universal gas constant, 1543 ft. - lb./(lb mole - ^oR)
T	Absolute Temperature, ^oR
t	Time, hr.
u	Viscosity, lb./(ft. - hr.)
V	Volume of pressure vessel, ft^3
v	Volume, ft^3

The perfect gas expression which relates the pressure, temperature and volume of a perfect gas is expressed as

$$Pv = nRT \qquad (2)$$

The experimental procedure used to determine the permeability of coal refuse briquettes consisted of using a briquette as a plug in a pressure

vessel and determining the pressure within the vessel as a function of time. This is an unsteady state operation in which the pressure driving force is continually changing with time; therefore, a mass balance on the gas contained in the vessel yields

$$\frac{dn}{dt} = -NA \tag{3}$$

where A is the area through which gas flow is occurring.

Expressions (1) to (3) form the basis of the mathematical treatment required to determine permeability. Substituting equation (1) into (3) yields

$$\frac{dn}{dt} = -\frac{d^2 g\, A}{32\, u l RT} P_a (P_1 - P_2) \tag{4}$$

Taking the differential of the ideal gas law, equation (2), with dv = 0 results in $dn = Vdp_1/RT$ and substituting this expression into (4) yields

$$\frac{dP_1}{dt} = -K \frac{P_1 + P_2}{2} (P_1 - P_2) \tag{5}$$

where $K = A\, d^2 g/(32\, Vul)$
Rearranging equation (5) results in the following expression relating the pressure within the vessel P_1 to time t:

$$\int_{P_o}^{P_1} \frac{d P_1 P_1}{P_2^2 - P_1^2} = \frac{K}{2} \int_0^t dt \tag{6}$$

where P_o is the initial pressure in the vessel at time t = 0. Intergrating the above expression between the indicated limits yields the following relationship between the chamber pressure P_1 and t:

$$\ln \frac{\frac{P_2 + P_o}{P_2 - P_o}}{\frac{P_2 + P_1}{P_2 - P_1}} = K P_2 t \tag{7}$$

Expression (7) is used to determine K since experimentally P_1 is known as a function of time. The parameter K is determined as the slope of

$$(P_2 + P_o/P_2 - P_o)/(P_2 + P_1/P_2 - P_1) \text{ vs } t$$

By definition, the permeability of a porous solid is the rate of diffusion per unit pressure gradient across the solid. The permeability P can be defined using the following expression for which P has the units of $ft^3/hr - ft^2 - (lb/ft^2/ft)$ and z is the depth of the porous solid in the direction of flow.

$$P = (N\ RT/P_a)/(P_1 - P_2/z) \tag{8}$$

Substituting expression (1) into (8) yields a relationship between the parameter K and permeability:

$$P = \frac{KVz}{A} \tag{9}$$

Since K is known from (7) and V, z, and A are known, the permeability can be established using expression (9).

Freeze-Thaw Testing of Coal Refuse

The freeze-thaw experiments were conducted using a refrigerator in which the refrigeration area was at 34°F and the freezing compartment at 3°F.

To initiate the freeze-thaw test, 5 briquettes each of -10, -20, and -60 mesh unburnt bituminous coal refuse briquettes were soaked in 34°F water about 3 hours and then placed in the freezing compartment overnight. The freeze-thaw test required a rigid schedule in order to make the results meaningful. This schedule is presented in Table IX.

TABLE IX

Schedule of Freeze-Thaw Test

	Time	Event
	9:00 a.m.	Remove from freezing compartment. Place in thawing water.
Complete Cycle	9:45 a.m.	Remove from thaw water. Place in freezing compartment.
	12:45 p.m.	Remove from freezing compartment. Place in thawing water.
Complete Cycle	1:30 p.m.	Remove from thawing water. Place in freezing compartment.
	4:30 p.m.	Remove from freezing compartment. Place in thawing water.

TABLE IX CON'T

Schedule of Freeze-Thaw Test

	Time	Event
Complete Cycle	5:15 p.m.	Remove from thawing water. Place in freezing compartment.

A freeze-thaw cycle consists of one thawing operation, and one freezing operation. After 10 of these cycles, one of each of the 3 different kinds of briquettes was removed from the system and allowed to air dry for 1 to 2 days. The compressive strength of these samples was then determined. This procedure was repeated at 20, 25, 30 and 35 cycles. The data obtained was the compressive strength as a function of the number of freeze-thaw cycles for each kind of briquette.

BIBLIOGRAPHIC: Applied Technology Div. Carbonate Bonding of Coal Refuse, EPA Grant No. 14010FOA

ACCESSION NO:

A laboratory study of the variables which effect carbonate bonded coal refuse has been made. The carbonate bonding of coal refuse consists of mixing coal refuse with water and lime hydrate, compacting the mixture, and reacting it with a carbon-dioxide-rich gas to form a coherent structure bonded by a matrix of calcite crystals. Carbonate bonded coal refuse can be used in road building or as a coal refuse pile sealant to minimize acid mine water pollution.

Four types of coal refuse were investigated. Compressive strengths of

Key Words

Carbonate Bonding, Coal Refuse, Coal Refuse Binder, Refuse Pile Sealant, Pollution Abatement, Road Building

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2200 to 4400 psi were obtained for the coal refuse investigated using up to 12 percent lime hydrate and 9 to 15 percent water. In general, the compressive strength of the carbonate bonded coal refuse increases with increasing lime hydrate content, reaction time and carbon dioxide concentration in the carbonate bonding reaction gas. The air and water permeability of carbonate bonded coal refuse was comparable to concrete.

An approximate cost comparison between carbonate bonded coal refuse and other construction materials indicated that the carbonate bonding process utilizing coal refuse is the least cost means for coal refuse pile sealing and road building.

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23 Descriptors (Starred First)

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27 Abstract A laboratory study of the variables which affect the properties of the carbonate bonded coal refuse has been made. The carbonate bonding process utilizing coal refuse as a fill material consists of mixing coal refuse with water and lime hydrate, compacting the mixture, and reacting it with a carbon-dioxide-rich gas to form a coherent structure bonded by a matrix of calcite crystals. The resulting carbonate bonded coal refuse can be used in road building or as a coal refuse pile sealant to minimize acid mine water pollution.

Four types of coal refuse were investigated--a relatively unoxidized and highly oxidized bituminous coal refuse and a relatively unoxidized and highly oxidized anthracite coal refuse. It was found that compressive strengths of 2200 to 4400 psi were obtained for the four types of coal refuse investigated using up to 12 percent lime hydrate and 9 to 15 percent water. In general, the compressive strength of the carbonate bonded coal refuse increases with increasing lime hydrate content, reaction time and carbon dioxide concentration in the carbonate bonding reaction gas.

The air and water permeability of carbonate bonded coal refuse was found to be comparable to concrete. An approximate cost comparison between carbonate bonded coal refuse and other construction materials and techniques indicated that the carbonate bonding process utilizing coal refuse is the least cost means available for coal refuse pile sealing and road building.

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